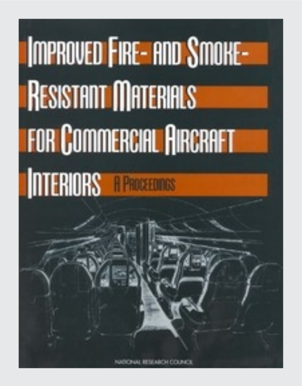

Improved Fire- and Smoke-Resistant Materials for Commercial Aircraft Interiors: A Proceedings

DETAILS

258 pages | 8.5 x 11 | PAPERBACK
ISBN 978-0-309-05336-5 | DOI 10.17226/4970

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Improved Fire- and Smoke-Resistant Materials for Commercial Aircraft Interiors

A Proceedings

Committee on Fire- and Smoke-Resistant Materials for Commercial Aircraft Interiors
National Materials Advisory Board
Commission on Engineering and Technical Systems
National Research Council

Publication NMAB-477-2

NATIONAL ACADEMY PRESS
Washington, D.C. 1995

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This study by the National Materials Advisory Board was conducted under Grant No. FAA-93-G-033 with the U.S. Department of Transportation.

Library of Congress Catalog Card Number 95-70653
International Standard Book Number 0-309-05336-6

Available in limited supply from:
National Materials Advisory Board
2101 Constitution Avenue, NW
HA-262
Washington, D.C. 20418
202-334-3505

Additional copies are available for sale from: National Academy Press 2101 Constitution Avenue, NW Box 285 Washington, D.C. 20055 1-800-624-6242 (202) 334-3313 (in the Washington metropolitan area)

Printed in the United States of America.

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PREFACE

The Federal Aviation Administration (FAA) has established an Advanced Fire Safety Materials Research Program to meet the requirements of the Aviation Safety Act of 1988. The program's objective is "to discover the fundamental relationships between the composition and structure of materials and their behavior in fires to enable the design of a totally fire-resistant cabin for future commercial aircraft. Research will be basic in nature and will focus on synthesis, characterization, modeling, and processing of new materials and materials combinations to improve the fire performance, increase the functionality, and reduce the cost of next-generation cabin materials."

The FAA requested that the National Research Council, through its National Materials Advisory Board, recommend research in promising areas based on projected technology. Towards this end, the National Research Council established the Committee on Fire and Smoke Resistant Materials for Commercial Aircraft Interiors.

The committee hosted a Conference on Fire and Smoke Resistant Materials held at the National Academy of Sciences on November 8-10, 1994. Conference attendees included representatives from industry, government, and academe. These are the proceedings of that conference.

The conference participants identified trends in aircraft fire safety and suggested promising research directions for the FAA's program in smoke and fire-resistant materials. This conference report contains the 15 papers presented by the invited speakers and summaries of the workshop sessions that followed. The papers served as background for the workshop sessions, each of which addressed a specific topic:

(1) toxicity issues,
(2) fire performance parameters,
(3) drivers for materials development, and
(4) new materials technology.

Each workshop group discussed the current state of development, technological needs, and promising technology for future development. The workshop chairs reported on each session to the conference as a whole, after which issues of interest were further discussed by all participants.

The information from the conference presentations and workshop sessions have been used by the study committee as input to its final report.

The efforts of all the attendees, presenters, workshop chairs, and committee members and staff (and in particular Tom Munns) are acknowledged and appreciated.

ELI M. PEARCE
COMMITTEE CHAIR

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PART I

INVITED PAPERS

Federal Aviation Administration Fire Safety Mission

*Thomas E. McSweeny**

Aircraft fire safety has always been an issue of high priority with the flying public. As the agency with prime responsibility for aviation safety, the Federal Aviation Administration (FAA) continuously endeavors to maintain and enhance fire safety. These attempts include ensuring the safety of new aircraft designs through the certification process, of new aircraft in production through manufacturing inspection, and of aircraft in use through strict maintenance and inspection requirements. All attempts involve enforcement of standing safety requirements as laid down in the Federal Aviation Regulations and elaborated upon in a variety of documents, such as Aerospace Recommended Practices, Advisory Circulars, and technical reports. These requirements are kept technologically current by dozens of ad hoc committees operating under the aegis of organizations like the Society of Automotive Engineers.

In addition to the standing regulatory requirements, new standards for aircraft fire safety are periodically imposed. In the case of an immediate and known threat to safety, FAA certification authorities issue Airworthiness Directives. These require modification of specific aircraft models that have a feature identified as a safety threat. Occasionally, aircraft accidents or tests allow the FAA to pinpoint an area where a new fire safety requirement could offer demonstrable safety improvements for all aircraft of a given size or class. Such new requirements are established through a formal public rule-making process. FAA fire safety research and development, as well as test and evaluation, have traditionally been directed to support the rule-making process for near-term attainable improvements. Such work has also served to screen out unproductive or counterproductive regulatory endeavors whose deficiencies are identified in full-scale testing.

At the present time, major near-term fire safety research and development efforts are aimed at Halon® replacement, fuselage burnthrough resistance, onboard cabin water-spray systems, cargo compartment protection, and flight data recorder fire resistance. These near-term activities have resulted in the technical basis for many fire safety design considerations.

The FAA's role in air transport safety has been fundamentally modified through the provisions of the Aviation Safety and Research Act of 1988. This legislation has charged the FAA with the new mandate of carrying out long-term, basic research in many areas. These include not only improvement of fire safety but also how to deal with the safety of operating aging aircraft; how to understand human factors issues involving flight crews, aircraft mechanics, and air traffic controllers; and how to develop an air traffic control system to handle future fleet growth safely. Such long-range research offers the FAA a new dimension to our responsibilities of promoting a safe aviation system. It presents the FAA with organizational challenges such as obtaining resources, identifying the most productive research directions, and integrating this work into the FAA safety processes.

In the specific area of fire safety, which is the subject of this conference, the FAA has developed a plan or framework for initiatives with a longer-term safety payoff. A successful

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* Director, Aircraft Certification Service, Federal Aviation Administration, Washington, D.C.

long-term fire research program will provide the FAA with the third leg of a platform to provide a stable basis for future fire-safe aircraft. Rulemaking and Airworthiness Directives have proven their worth in the fire safety record of today's aircraft. The flying public demands that tomorrow's record be even better, and the FAA hopes that the results of this fire safety research effort will provide quantum improvements over today's technology.

This research framework includes six major research thrust areas. They are

1. fire modeling;
2. vulnerability analysis;
3. fire-resistant materials;
4. improved systems;
5. advanced suppression; and
6. fuel safety.

These areas were identified through consultations with technical experts throughout the country and together represent the FAA's view of the best comprehensive approach that could be followed with unconstrained resources. Of these fire safety research areas, fire-resistant materials is the topic on which the Congress has placed its greatest emphasis, and coincidentally it is the one area of the six that was rated highest in priority by FAA certification personnel. Consequently, this is the first area for which the FAA has sought full funding.

The quest for cabin interior materials that are more fire-resistant poses considerable challenges. In only a very superficial sense can an aircraft cabin interior be compared with other inhabited structures. While the major function of a building structure is for self-support, aircraft fuselage structural loads are dominated by the pressure differential between the interior and the low pressures found at high altitudes. Whereas building insulation is rated for its characteristics of thermal protection, aircraft insulation has a primary sound-absorbing function. This list of unique selection criteria can go on, but the importance of low weight for all elements making up the aircraft cabin interior can never be underestimated. It is for this reason that new fabrics had to be developed to provide means to fire-block aircraft passenger seats to satisfy new fire safety standards.

In a modern jet transport, the sidewall panels, partitions, ceiling, and stowage bins are typically honeycomb composite assemblies with Nomex® core, phenolic-impregnated fabric facesheets, and decorative layers of inks and thermoplastics. Seat covers are typically wool/nylon blends, while the fire-blocking layer may be polybenzimidazole, or a blend of Nomex® and Kevlar®. Seat back trays are typically molded polycarbonate. Overhead passenger service units can be of metal or Declar® construction. Windows are stretched acrylic, while carpets are wool or nylon. Floor panels might be of honeycomb construction with a Nomex® core and epoxyimpregnated graphite facings. The insulation behind the interior panels is fiberglass bagged in Mylar® liners. Cargo liners might be polyester or epoxy-impregnated fiberglass. Graphite fabrics are gradually moving in as lighter-weight replacements for fiberglass within the cabin. Polymers play a major role in the construction of aircraft interiors due to their many remarkable properties, which allow for a variety of desired end properties, ranging from weight and durability to comfort and aesthetics.

A number of fire safety considerations are involved with airplane design, certification, and operation. Engines, as well as auxiliary power units, include fire-detection and extinguishing systems. Wing fuel vents have flashback arrestors to minimize lightning hazards. Designated engine firewalls and flammable fluid-hose assembly designs must pass specified fire-endurance tests. Ducts carrying heated air from engine compressors have associated hot-air leak detectors for hot-air leaks. The routing of flammable fluid lines avoids areas having potential ignition sources. Main landing gear wheels are braked to a stop after lift-off to prevent damage to hydraulic systems from thrown tire belts. Landing gear tires are pressurized with nitrogen to prevent auto-ignition of tire pyrolyzate resulting from overheated brake mechanisms. Wiring within the airplane pressure vessel employs low-flammability insulation like Kapton®. Circuit breakers further protect the wiring from overheat.

The basic philosophy for fire safety in materials design and selection involves one or more of four goals depending on the fire threat and required functional performance of the material. These goals are

1. low ignitability;
2. low heat release;
3. fire containment; and
4. fire endurance.

Low ignitability, as demonstrated by a modified Bunsen burner test, is a requirement for most aircraft interior materials. Seats, as well as cabin interior panels, must demonstrate low heat release in addition to the ignitability requirement. Seat cushions configured in a mock-up assembly are allowed a specified weight loss when exposed to direct flames from a 2-gallon-per-hour oil burner. Panels are limited in both peak and total allowable heat release as tested in the Ohio State University Rate of Heat Release Apparatus.

A fire containment requirement is imposed on cargo liner materials. The liners are expected to prevent cargo compartment fires from spreading beyond the confines of the compartment. For small compartments, fire control is achieved through oxygen starvation. In larger compartments, a detection and suppression system is deployed. In the former case, cargo liner integrity is needed to keep fresh air out of the compartment. In the latter case, the liner integrity is needed to keep in both the fire and the extinguishing agent. The test requirement for cargo liners also involves the use of a 2-gallon-per-hour burner. Fire containment clearly includes fire endurance as a necessary requirement.

Fire endurance is the goal of fire safety requirements for emergency escape slides. The fire test involves exposing slide fabric, stretched by pressurization, to a radiant source. The endurance of slide material to the radiant heat from a fuel fire is enhanced when the slide fabric has an aluminized coating.

Additional aircraft cabin fire safety features include lavatory smoke detectors and trashbin extinguisher bottles, mandatory hand-held extinguishers for onboard use, floor proximity escape path lighting, and protective breathing equipment for the cabin and flight deck crew.

Aircraft fire safety is a complex issue. Quantum safety improvements will require a joint effort between the FAA, the air transportation industry, and other interested and affected parties. To be successful in this effort, we in the FAA need your help to meet these new challenges.

This conference hosted by the National Materials Advisory Board is a beginning to get your input, and I am confident that the conference will be productive.

Airplane Accidents and Fires

Thomas M. Murray[*]

INTRODUCTION

Airplane fires prompt fear and concern for anyone associated with air transport. Those associated include the passengers and flight and cabin crews, as well as those who must eventually provide rescue functions and extinguish an airplane fire. Fortunately, the aviation community experiences few fires while in flight. Furthermore, those fires that do occur on the ground are typically preceded by another event: a hard landing ruptures a fuel tank; a long landing prompts a runway overrun; a premature landing causes excessive airplane damage; a controlled flight into terrain shatters an airplane upon impact; etc.

Due to the frequency of—and often repeated—preceding events, Boeing believes that the most effective safety strategy available today is to PREVENT ACCIDENTS. Many airplane accidents are preventable using current technology and preferred cockpit procedures. For instance, controlled-flight-into-terrain accidents are preventable through technology, the ground proximity warning systems, *and an appropriate response* to the warning.

From reviewing multiple accident records, Boeing as well as others in the commercial airplane transportation industry have determined that rarely is an accident the result of only one event. Rather, most, if not all, accidents occur through a chain of events. For instance, the hard landing is often preceded by an unstabilized approach; the unstabilized approach may occur due to air traffic control instructions, weather, or other traffic; or cockpit procedures developed by the airline may be inadequate for some circumstances. By focusing on these chains of events for accidents and developing accident prevention strategies applicable to various links in the chain, Boeing and members of the commercial airplane transportation industry have found, and continue to find, *multiple opportunities for interrupting the chain of events* leading to an accident (see Figure 1).

Fire certainly fits within the realm of a multiple-cause process. The only place on the airplane where fire is planned is within the combustion chambers of the engine. Otherwise, any other fire event on the airplane is unplanned and requires at least one "event or cause" to precede the fire.

The information in this review of aviation accident data with associated fires is broken into three parts. First, there is an examination of the commercial jet transport accidents from 1959 through 1993. This information is provided to offer a perspective regarding aviation accidents from a variety of causes. Then, the second part reviews how fire has influenced the accident record. This data is presented in a format similar to the overall commercial jet transport statistics to help individuals compare the frequency of fire-associated events with the variety of other causes of accidents. Fire details are also provided to enhance understanding of airplane fire-related accidents. Finally, the third part examines some specific fire scenarios to illustrate

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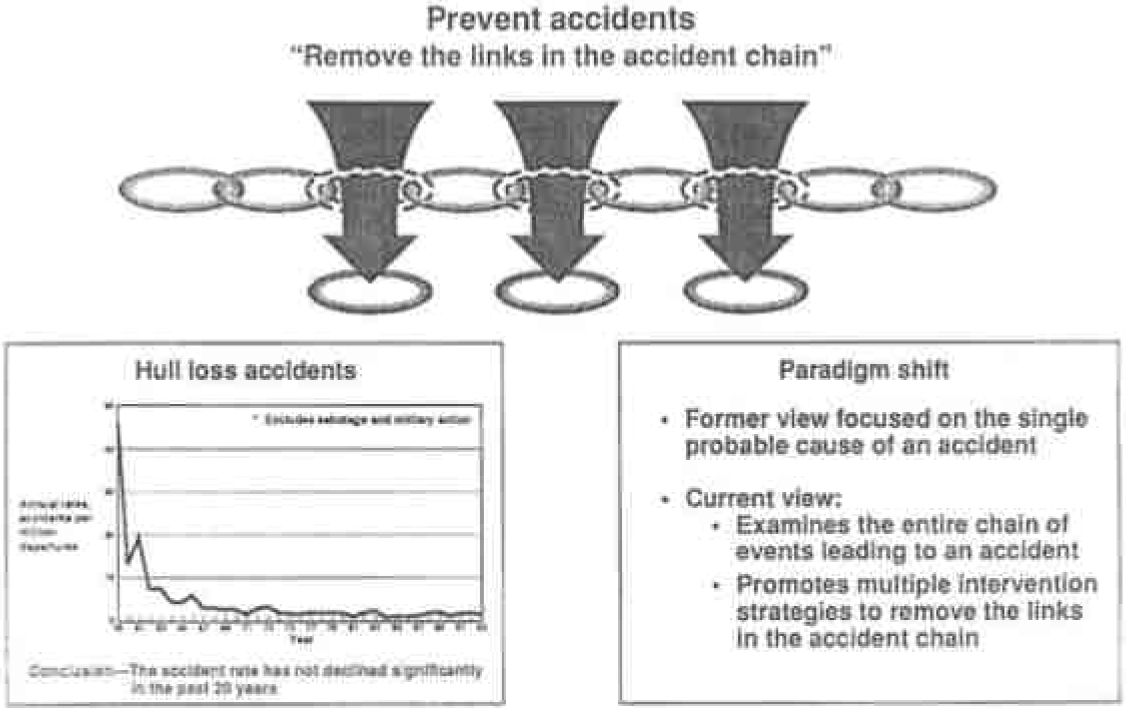
[*] Airplane Safety Engineering, Boeing Commercial Airplane Group, Seattle, Washington.

the range of events that occur, since looking at the number of events often fails to illuminate the many parameters associated with an aspect of aviation accident data, such as fire-related events. Moreover, these specific fire scenarios will also highlight the multiple-cause process and examine possible intervention opportunities where the outcome of the event might have changed considerably through alternative actions. In addition, these specific events have resulted in a range of outcomes despite some similar scenarios.



Prevent accidents

"Remove the links in the accident chain"

Hull loss accidents

Conclusion—The accident rate has not declined significantly in the past 20 years

Paradigm shift

- Former view focused on the single probable cause of an accident
- Current view:
  - Examines the entire chain of events leading to an accident
  - Promotes multiple intervention strategies to remove the links in the accident chain

FIGURE 1 Accident chain concept

COMMERCIAL JET TRANSPORT ACCIDENT STATISTICS

Background for Accident Data-Collection Processes

Boeing has collected accident data since 1959 for commercial jet operations with certified jet aircraft greater than 60,000 lb maximum gross weight. This data-collection effort has included not only Boeing airplane models but also data for a variety of competitor airplanes. Boeing believes that it must improve airplane safety using all available data sources; therefore, all catastrophic airplane accidents are reviewed.

For the accident information presented in this review, there have been some data exclusions. First, data for sabotage, military action/operation, and non-operational events are excluded. Non-operational events include those where the airplane is not in service; the airplane may be in a hangar for maintenance, on a ramp for overnight storage, etc. Relevant data includes passenger operations; all-cargo operations; and test, training, demonstration, and ferry flights. Furthermore, worldwide flight operations are included. However, accident data for airplane models from the countries of the former Soviet Union are excluded due to the lack of a complete accident record as well as a different and not well understood airplane certification process as compared with Federal Aviation Administration (FAA), Civil Aviation Authority, or Joint Aviation Authority certification processes.

To determine the flight time and cycles, data is collected by both the aircraft manufacturers and the engine companies. This data is gathered from operators' aircraft and engine logs.

Accident data are obtained, when available, from government accident reports. In addition, information is solicited from operators, manufacturers (both for the completed airplane product as well as for various systems and components), and various government and private information services. The accident selection criteria essentially corresponds to the U.S. National Transportation Safety Board's accident definition. However, events are excluded that involve nonfatal injuries resulting from maneuvering, atmospheric turbulence, loose objects, boarding or disembarking, or airplane servicing activities.

To fully understand the accident data that Boeing collects, it is important that the following definitions be relayed:

- *Aircraft accident* means an occurrence associated with the operation of an aircraft that takes place between the time any person boards the aircraft with the intention of flight until such time as all such persons have disembarked, in which any person suffers death or serious injury as a result of being in or upon the aircraft or by direct contact with the aircraft or anything attached thereto, or the aircraft receives substantial damage.
- *Serious injury* means any injury that (1) requires hospitalization for more than 48 hours, commencing within 7 days from the date of the injury received; (2) results in a fracture of any bone (except simple fracture of fingers, toes, or nose); (3) involves lacerations that cause severe hemorrhages or nerve, muscle, or tendon damage; (4) involves injury to any internal organ; or (5) involves secondor third-degree burns affecting more than 5 percent of the body surface.
- *Fatal injury* is defined as an injury that results in death within 30 days of the accident.
- *A hull-loss* means damage due to an accident that is too extensive to repair, or that, for economic reasons, was not repaired, so that the aircraft was not returned to service.
- *A survivable accident* is one in which the fuselage remains relatively intact, the crash forces do not exceed the limits of human tolerance, there are adequate occupant restraints, and there are sufficient escape provisions.

Boeing has accident data for 9 airplane manufacturers, which include data on 28 different model types. As of the end of 1993, there were 11,433 aircraft in service; 6,465 of these aircraft were Boeing models. From 1959 through 1993, the commercial jet transport industry had accumulated 406 million flight hours (237 million on Boeing aircraft) and 270 million departures (149 million on Boeing aircraft). Figure 2 provides visual information for both the number of airplanes in service and the annual departures since 1964.

Aviation Accident Data for Hull Losses and Fatalities

Hull-Loss Data

The aviation accident record, as measured by the number of hull losses each year, suggests that the aviation industry possesses an enviable safety record compared with other transportation modes. Overall, the worldwide commercial jet fleet has a hull-loss accident rate of approximately two accidents per million departures. Figure 3 displays the worldwide commercial jet fleet hull-loss accident rate per million departures for all airplane models. The total number of hull losses from 1959 through 1993 was 512. From 1984 through 1993, 171 hull losses occurred. Further specifics regarding the hull losses can be seen in Table 1.

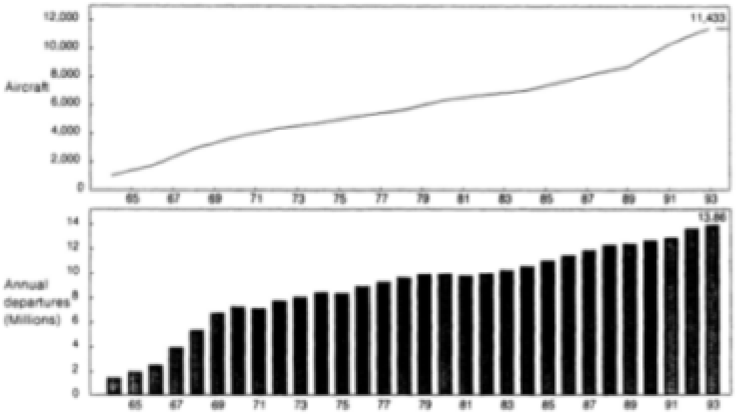


FIGURE 2 Jet aircraft in service and annual departures.

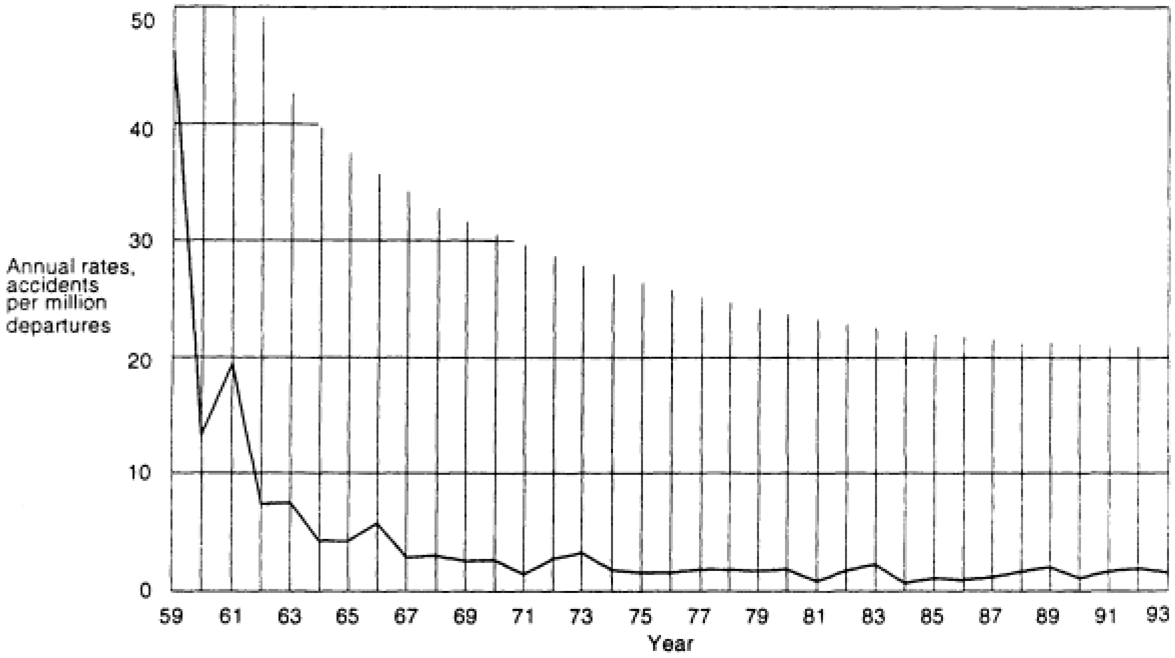


FIGURE 3 Hull-loss accidents (excludes sabotage and military action).

TABLE 1 Hull-Loss Accidents

1959-1993	1984-1993
512 hull losses	171 hull losses
U.S. operators	U.S. operators
· 97 during passenger operations	· 23 during passenger operations
· 27 during all-cargo operations	· 8 during all-cargo operations
· 16 during test, training, demonstration, or ferry	· 3 during test, training, demonstration, or ferry
Non-U.S. operators	Non-U.S. operators
· 295 during passenger operations	· 103 during passenger operations
· 43 during all-cargo operations	· 24 during all-cargo operations
· 34 during test, training, demonstration, or ferry	· 10 during test, training, demonstration, or ferry

From the hull-loss accidents chart (Figure 3), it appears that the commercial airplane transportation industry has significantly reduced the accident rate from its initially high level to a relatively low rate. However, *despite the low accident rate,* THE COMMERCIAL AIRPLANE TRANSPORTATION INDUSTRY MUST CONTINUE TO IMPROVE. Indeed, the Boeing goal, and now FAA-industry goal, is zero accidents. Consequently, Boeing has promoted the concept of "preventing accidents" as noted in the introduction.

Figure 4 shows why the current hull-loss accident rate is unacceptable. If the aircraft fleet continues to expand (and there are a number of reasons for expansion to continue: increased traffic in Asia, South America, and countries of the former Soviet Union; increased global business processes; increased leisure travel; etc.), then it is possible that the aviation industry could experience a hull-loss every week by the year 2010. Clearly, this possibility is unacceptable for the aviation industry.

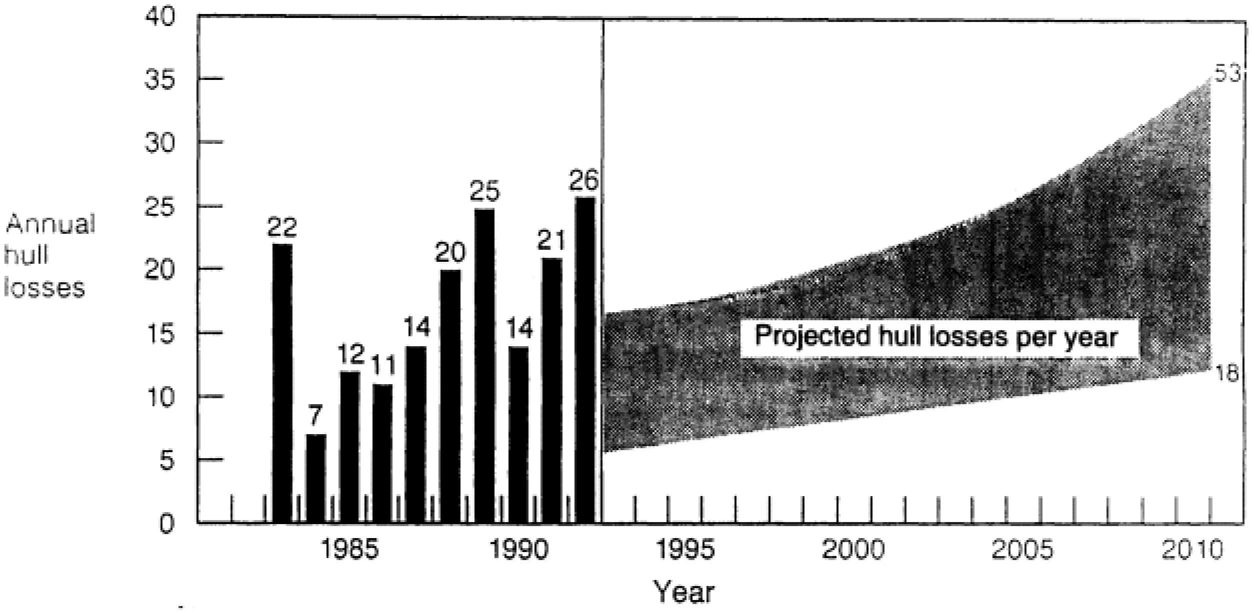


FIGURE 4 Projected hull-loss accidents based on accident rates for past 10 years and expected fleet growth.

Furthermore, some recent trends, as shown by a 5-year moving average of the hull-loss accident rate, suggest that those in the aviation industry must remain vigilant in the pursuit of zero accidents due to an apparent increasing hull-loss accident trend. (See Figure 5.)

From Figure 6, it appears that most of the newer-generation commercial jet transports are contributing favorably to the lower hull-loss accident rate. However, the overall accident rate is still 1.9 hull-loss accidents per million departures. This airplane generation assessment is further detailed by Figure 7. In this figure the hull-loss rates for various airplane generations, except for those airplanes from the first generation of commercial jet transports, are noted.

The aviation industry is not without guides or direction as to the types of accidents that occur and possible remedies. As Figure 8 shows, there are specific phases of flight where the majority of accidents occur. For instance, final approach and landing phases of flight account for more than 40 percent of the hull-loss accidents. On the other hand, these two flight phases represent only 4 percent of the total flight time. Due to this data and other indicators used by the airlines, many airlines have instituted specific final approach criteria. For instance, Boeing

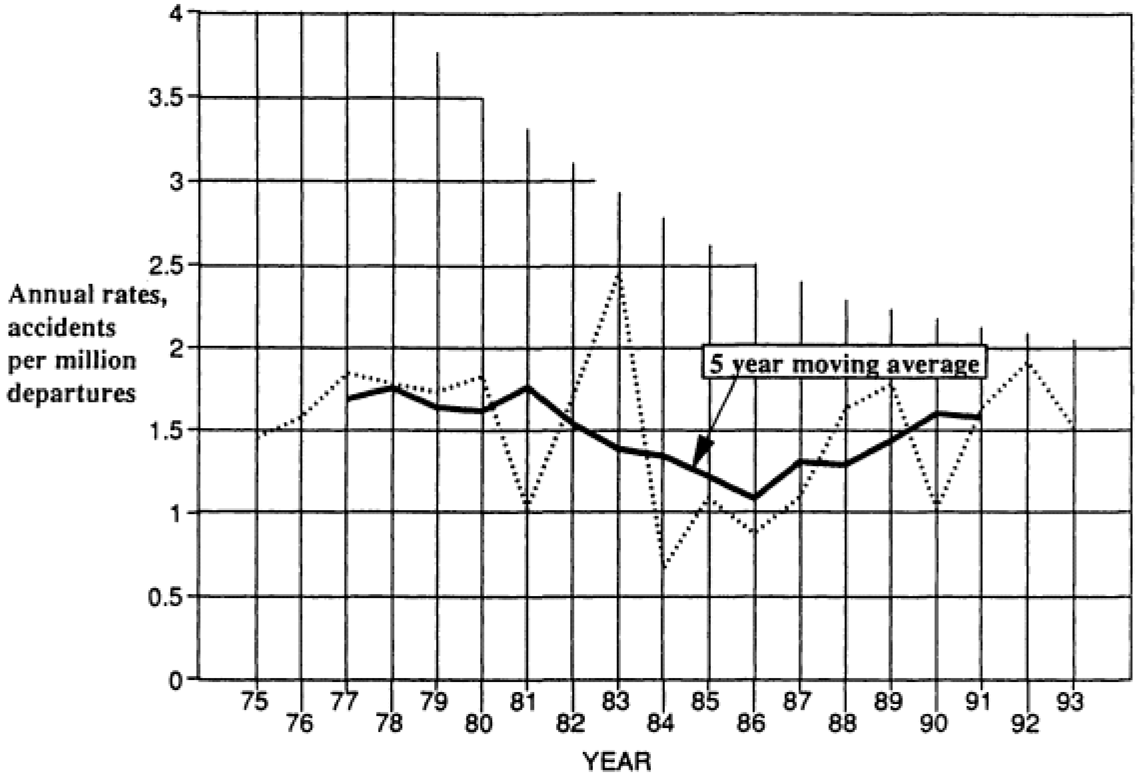


FIGURE 5 Five-year moving average of hull-loss accident rates (excludes sabotage, military action, and former Soviet Union airplane models).

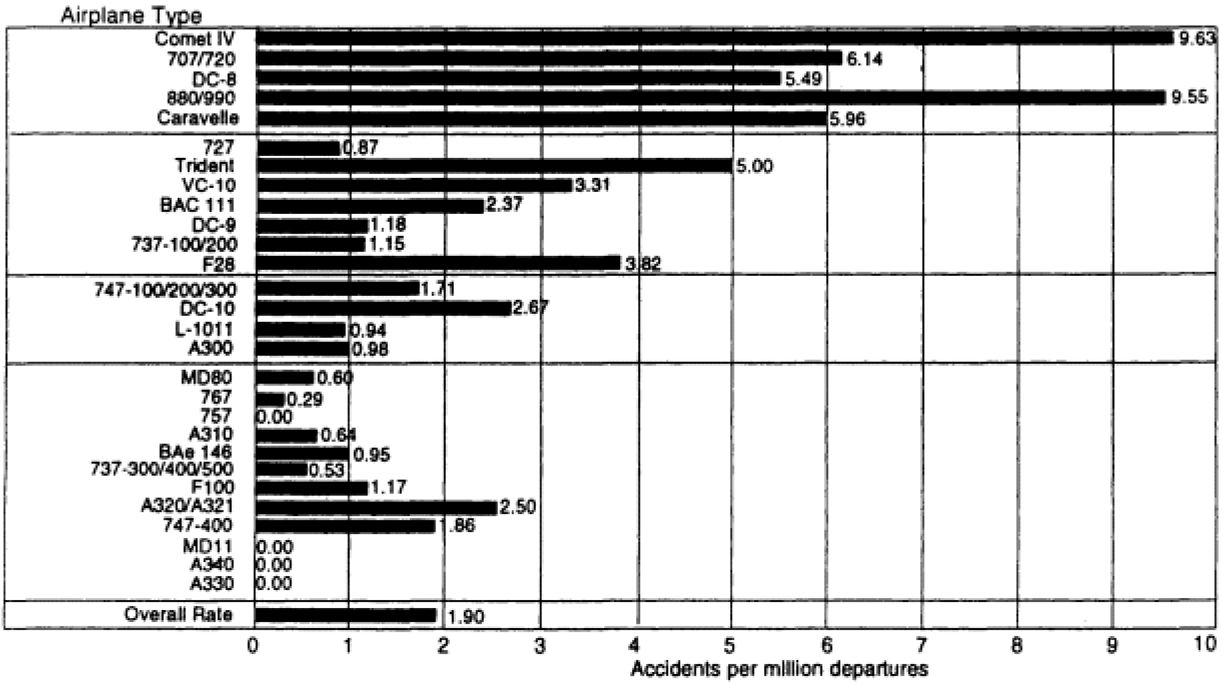


FIGURE 6 Hull-loss accident rates per generation of aircraft (excludes sabotage and military action).

recommends that a stabilized approach be achieved by 1,000 feet. Most airlines require a stabilized approach by at least 500 feet. If the airplane is not stabilized by 500 feet, most airlines that require the airplane to circle for another approach go-around. One airline that uses the 1,000-feet stabilized approach guideline as a requirement has never had an approach accident.

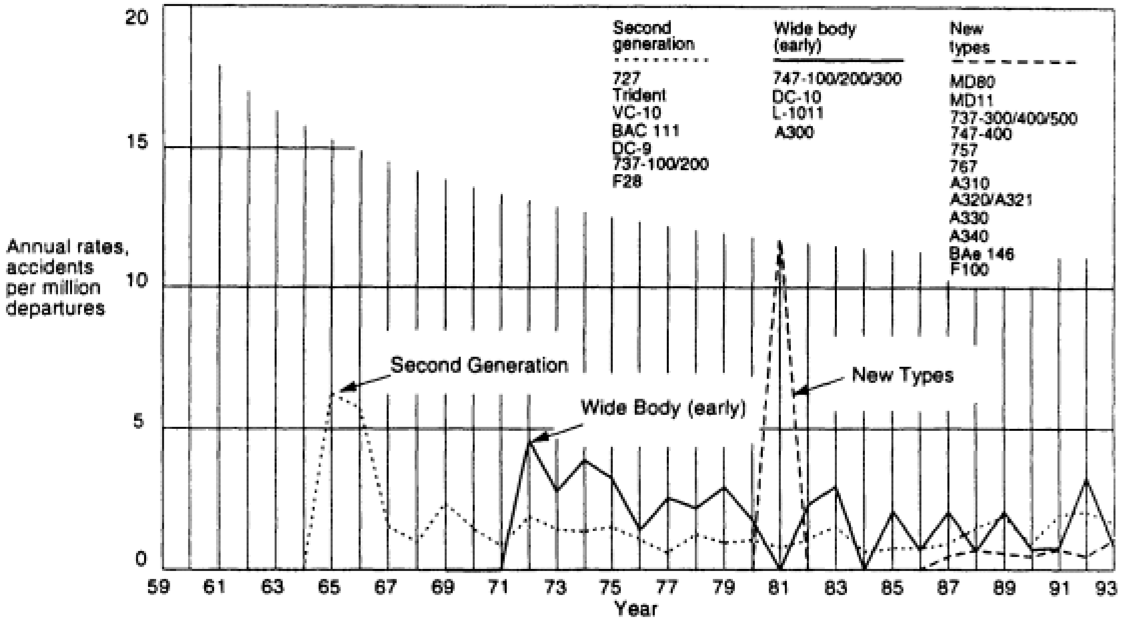


FIGURE 7 Hull-loss accident rates by generic group of aircraft (excludes sabotage and military action).

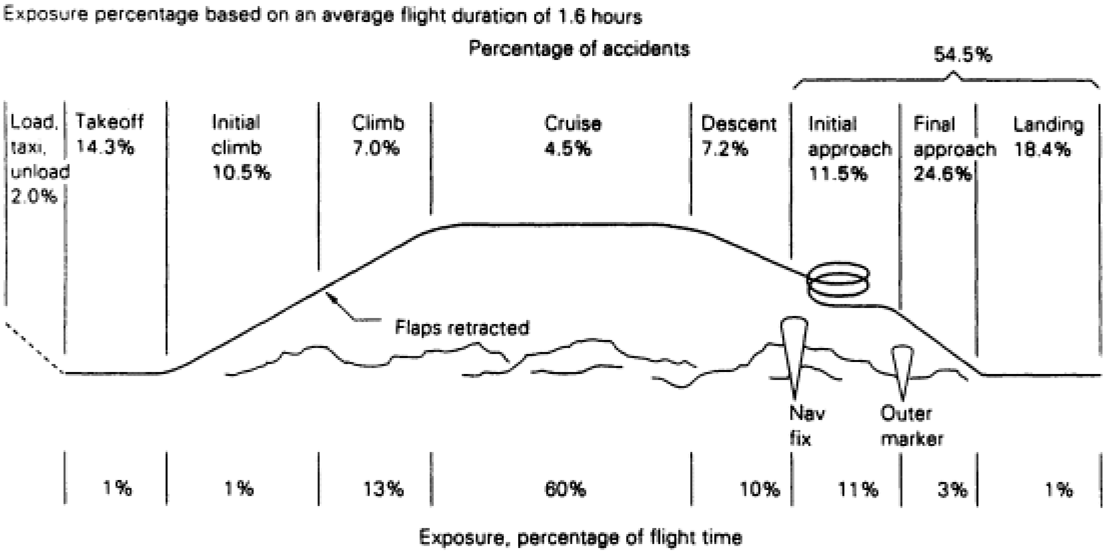


FIGURE 8 Hull-loss accident rates for specific phases of flight (excludes sabotage and military action).

Take-off and initial climb also represent an opportunity for improvement. Some 25 percent of the hull-loss accidents occur during this phase of flight. Some actions that have occurred include reinforcement of appropriate procedures for refused take-off decisions. For instance, Boeing airplanes purposely disallow some messages from getting to the flight deck during the take-off phase to prevent the pilots from being distracted by airplane functions that do not affect the flying capability of the airplane.

As shown in Figure 9, the non-U.S. operators still have a higher accident rate than the U.S. Operators.

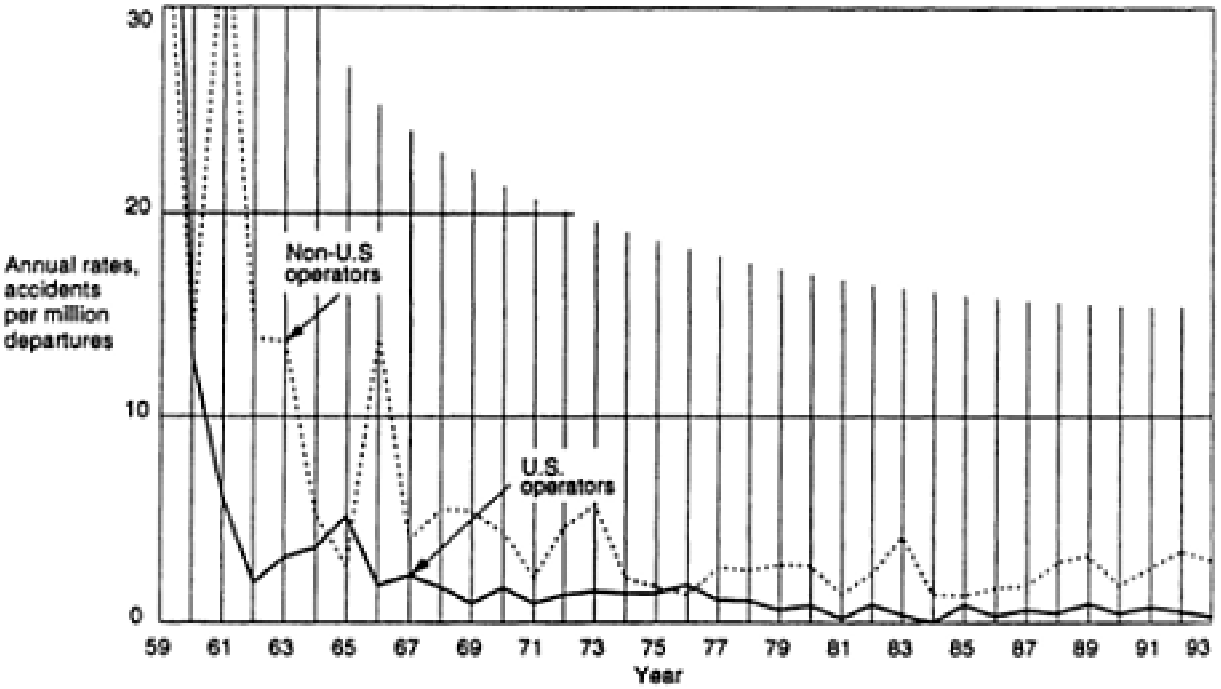


FIGURE 9 Hull-loss accident rates, U.S. and non-U.S. (excludes sabotage and military action).

Fatality Data

Hull-loss data is not the only measure of airplane safety processes. Another measure used by Boeing and many airlines is the number of fatal accidents that occur. This measure is useful, since many hull-loss accidents do not result in fatalities. Table 2 shows a breakdown of the 398 fatal accidents that occurred from 1959 through 1993.

Figure 10 shows that the fatality rate has declined from its initial high rate. However, the number of fatalities per year does not show a similar decline.

As shown in Figure 11, there are particular events that have prompted the most fatalities. Controlled flight into terrain (CFIT) remains a dominant cause of fatalities despite the introduction of Ground Proximity Warning Systems, improved crew procedures, and continuous training.

TABLE 2 Breakdown of Fatal Accidents

1959-1993	1984-1993
398 fatal accidents	120 fatal accidents
Passenger operation	Passenger operation
· 319 fatal accidents	· 96 fatal accidents
· 18,956 fatalities*	· 5,397 fatalities*
All-cargo operation	All-cargo operations
· 44 fatal accidents	· 18 fatal accidents
· 174 fatalities*	· 76 fatalities*
Test, training, demonstration, and positioning	Test, training, demonstration, and positioning
· 35 fatal accidents	· 6 fatal accidents
· 168 fatalities*	· 53 fatalities*

* Onboard fatalities only.

Despite the low accident rates, any fatalities are unacceptable to all aviation participants. The aviation industry must continue to find ways of interrupting the accident chain to PREVENT ACCIDENTS.

COMMERCIAL JET TRANSPORT FIRE STATISTICS

Recall that Figure 3 shows the worldwide hull-loss accident rate. Similar information for fire-related hull-loss accidents follows. The fire-related hull-loss accidents were divided into two categories: those hull-loss events where the fire was the primary cause of the hull-loss and those events where some other event preceded the fire, thus fire was a secondary event. "Primary fire-related hull-loss events" include cargo compartment fires, lavatory fires, fuel tank fires, engine fires, engine burst, etc. For primary fire events, the events were screened with the following criteria: "If the fire had not occurred, would a hull-loss not have resulted?" If the answer to this question was yes, then fire was the primary cause. (Engine burst was included in the primary category despite the screening criteria, since flight crews have minimal control of the engine burst phenomenon.) "Secondary fires" include such events as a hard landing where the landing gear subsequently punctures the fuel tank, CFIT with resulting fire, refused take-off events where the wings are sheared after the airplane goes off the end of the runway, etc. Secondary events include all the events not placed into the primary category.

Given these two categories, the fire-initiated hull-loss accident rate is 0.1 per million departures. The non-fire-initiated hull-loss accident with fire rate is 0.7 per million departures. Figure 12 displays this data along with the overall accident rate. The fire-caused hull-loss accident rate, or primary category, is plotted in Figure 13 for 1959 through 1993.

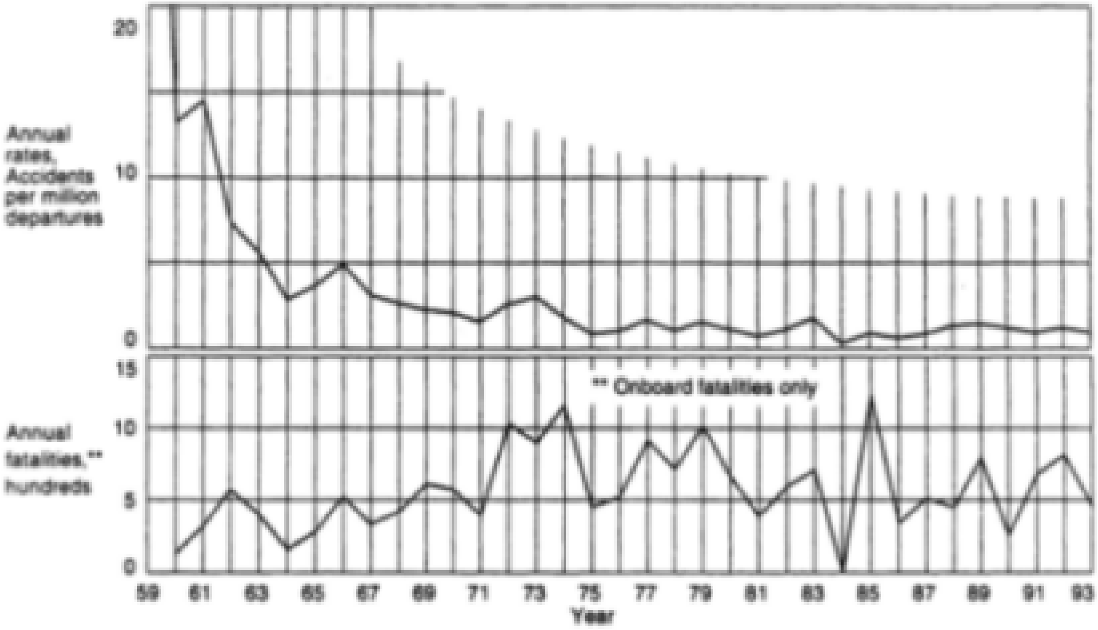


FIGURE 10 Fatal accidents, annual rates, and annual fatalities (excludes sabotage and military actions).

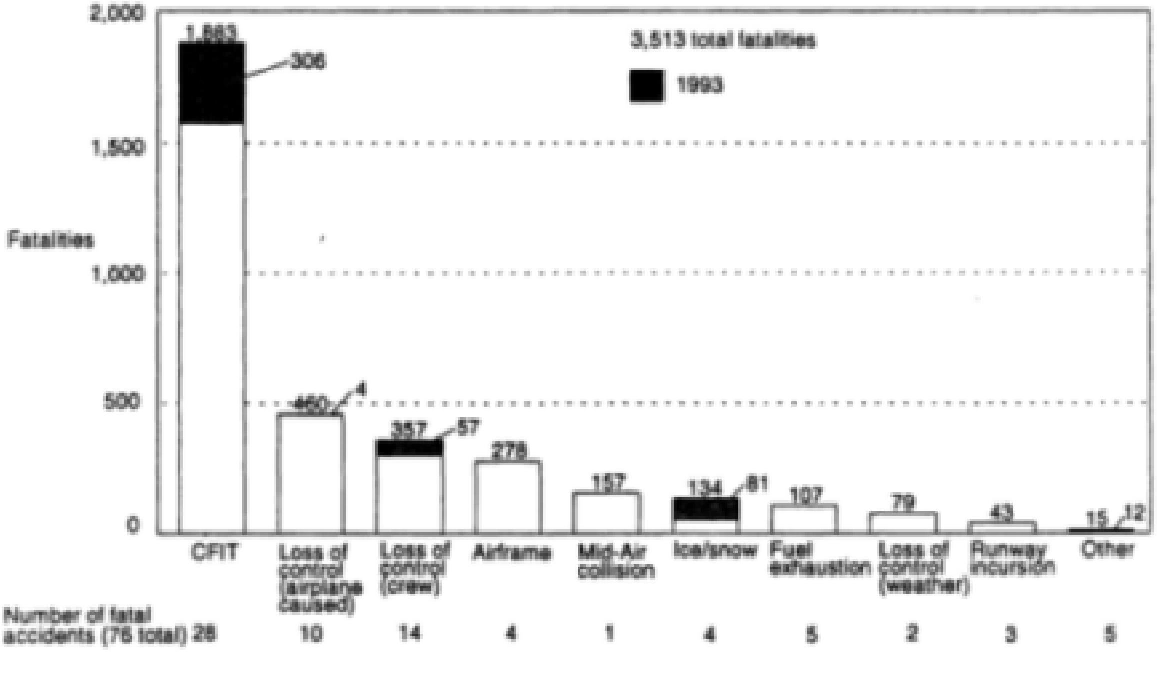


FIGURE 11 Worldwide airline fatalities (excludes sabotage and military action).

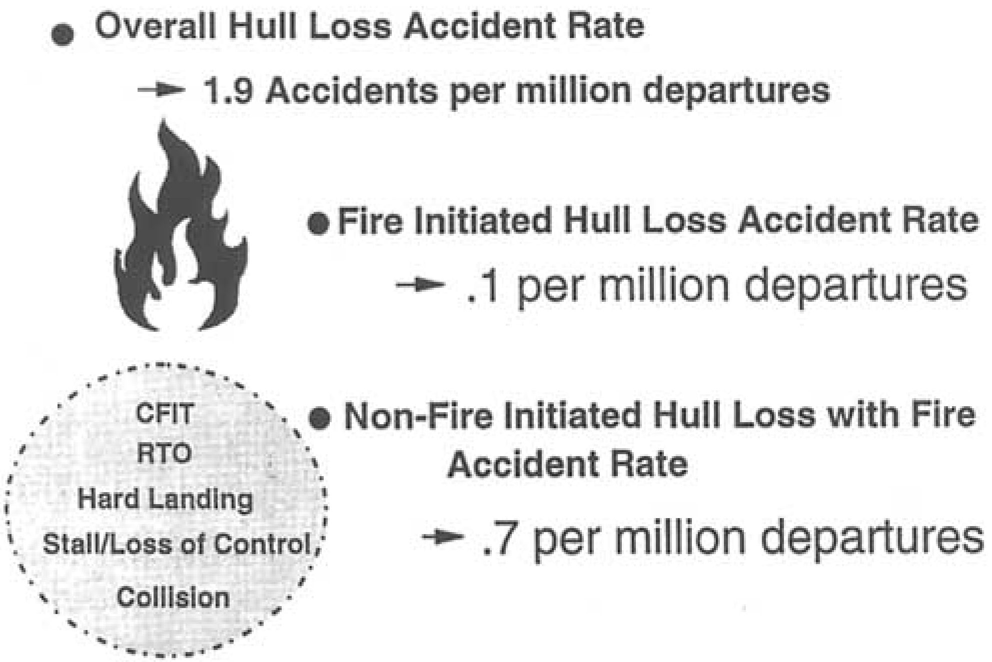


FIGURE 12 Overall hull-loss accident rates and fire

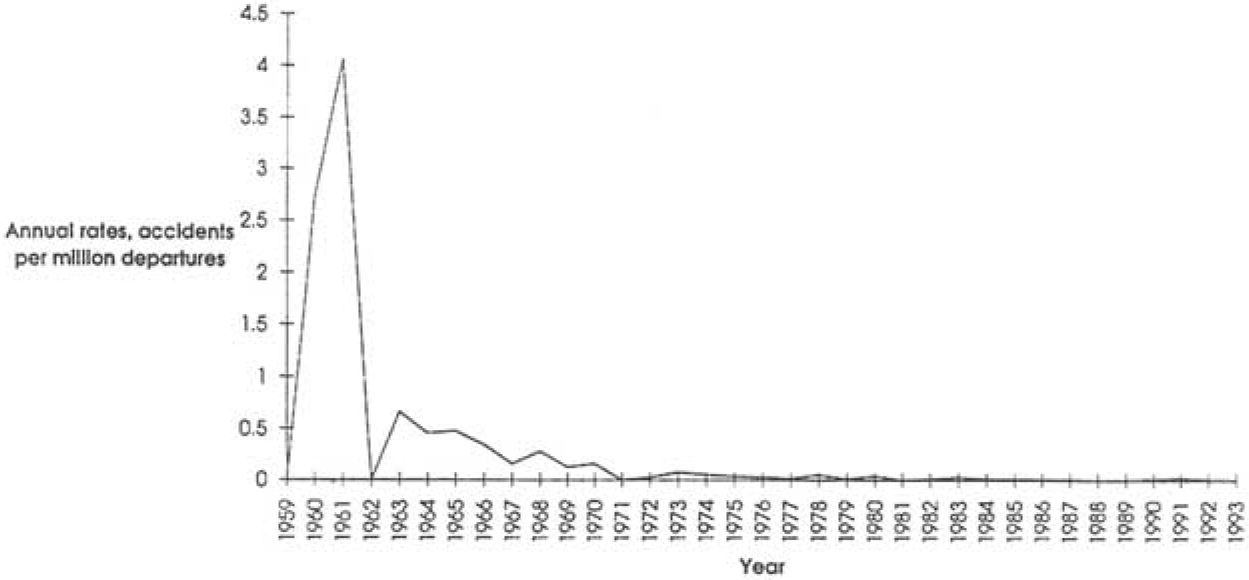


FIGURE 13 Fire-caused hull-loss accident rates.

Of all of the hull-loss accidents with fire, only 11 percent of these events were initiated by fire or in the "primary" category. Indeed, the remaining 89 percent of these hull-loss accidents with fire were preceded by some other significant event, as shown in Figure 14 with details on the contributors to both the fire-initiated and non-fire-initiated hull-loss accidents.

Of the total number of fatalities from 1959 through 1993, only 19 percent were killed by the fire via burns, smoke inhalation, asphyxiation, or heat. Although many fatalities occur with fire-related events, a number of these fatalities are caused by impact injuries (see Figure 15). Annual fire- and smoke-caused fatalities are shown in Figure 16.

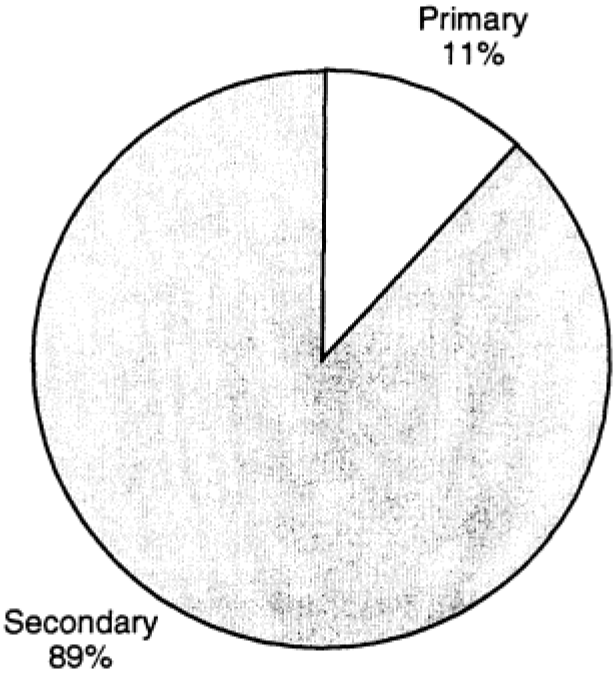


FIGURE 14 Fire-initiated versus non-fire-initiated events for all hull-loss events associated with fire.

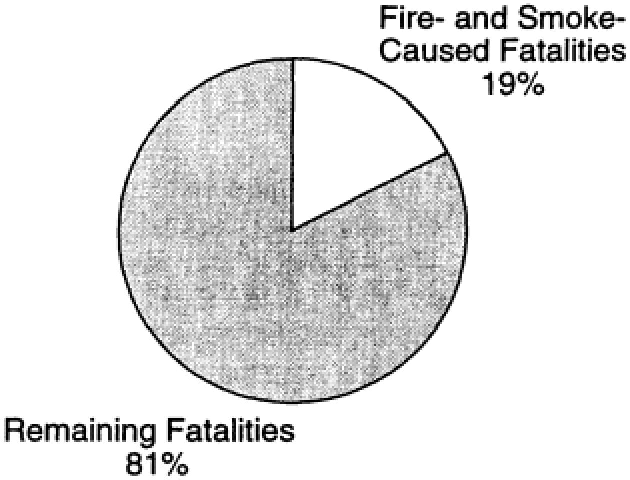


FIGURE 15 Total fatalities and the percent of fire- and smoke-caused fatalities.

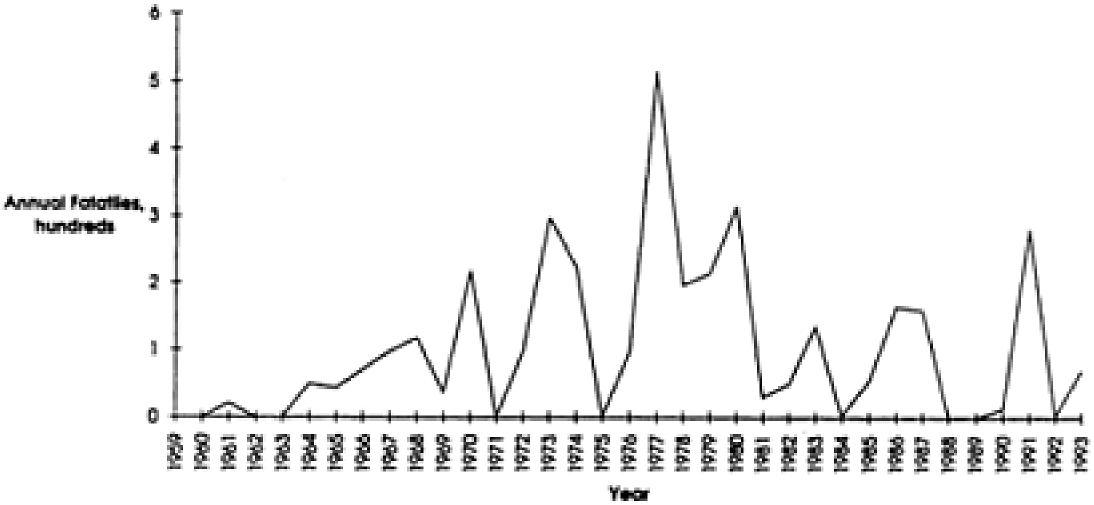


FIGURE 16 Annual fire-smoke-caused fatalities.

SELECTED FIRE SCENARIOS

Although the statistics provide very detailed information regarding fire events, some sample scenarios also reveal the diverse nature of the fire event. Therefore, summaries of four different hull-loss accidents where fire occurred are provided. Event sequences are provided for each accident to help readers focus on the chain of events preceding the accident.

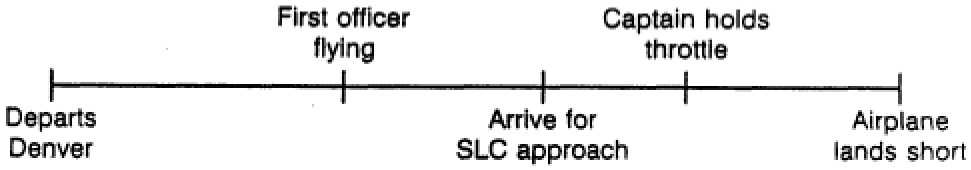
The key message from these example accidents is that most, if not all, airplane accidents are a chain of events. Therefore, these chains contain multiple opportunities to interrupt the accident scenario.

Example: 727, Salt Lake City

The airplane had originally departed New York and landed in Denver (see Figure 17). The captain had flown that segment. The first officer was flying the Denver to Salt Lake City segment. The airplane arrived within the Salt Lake approach area south of Provo, Utah. Although it was dark, it was typical Utah weather: VFR (visual flight rules) to 11,000 feet Normally, the captain preferred to descend prior to Provo, but that night the descent was delayed momentarily. Eventually, the first officer started the descent. To meet the threshold appropriately, the descent was motivated such that the airplane showed descent rates greater than 2,000 feet/minute. Company policy was to descend at 600 to 800 feet/minute. Prior to the threshold, the first officer moved his hand to the throttles to arrest the descent. The captain restrained the first officer. The flight engineer reported later that he, too, felt that the descent needed to be arrested. The descent continued. The airplane landed 335 feet short of the runway with a descent rate of 2,300 feet/minute. Despite the hard impact, the airplane remained relatively intact. Although the impact injuries were not excessive, many individuals were killed by fire-related agents: smoke, fire, and lack of oxygen.

Again, there were multiple opportunities for altering the chain of events. First, the air traffic control center needed greater understanding of the preferred airplane descent profiles. Although airplanes can lose altitude very quickly, accelerated descents not only affect safety but also affect airplane engine life. Next, the cockpit communications environment needed to utilize the capability and recognize the concerns of all the flight crew members. One the outcomes of this accident was to develop and promote the concept of *cockpit resource management:* all flight crew members offer input while still allowing the captain to maintain his or her role as final decision maker.

- Accident profile
  - November 11, 1965
  - 727 model
  - Salt Lake City
- Fatalities: 43
  - 85 passengers
  - 6 crew
- Chain of events



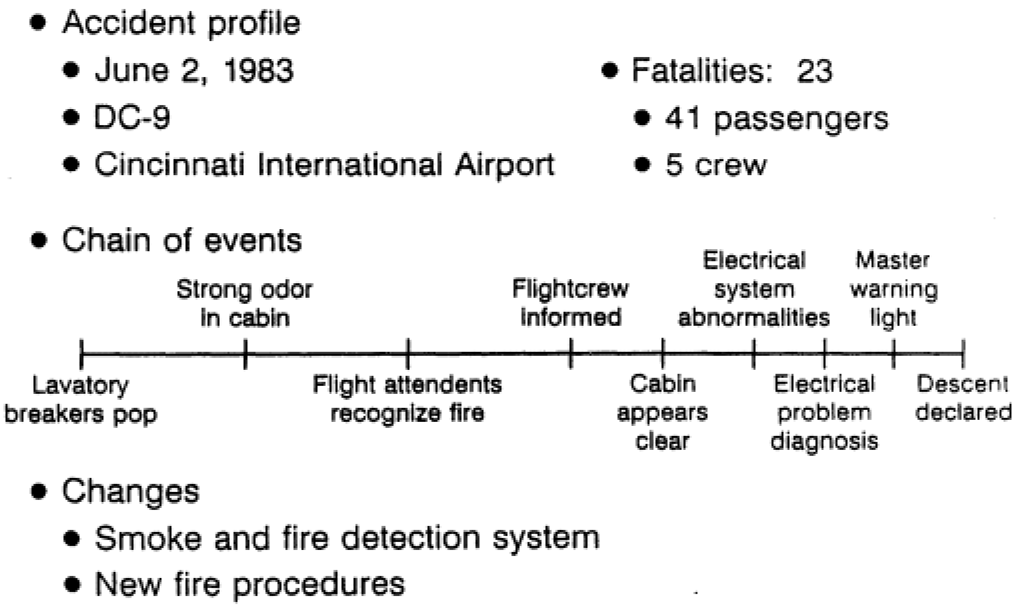
- Change
  - Procedures training for flightcrews

FIGURE 17 Lessons learned, 727 Salt Lake City accident. NOTE: Timelines not to scale.

Example: DC-9, Cincinnati

The airplane had departed Dallas and was enroute to Toronto (see Figure 18). At 1851 the lavatory breakers popped on the flight deck. The flight crew tried multiple times to reset the breakers. There was no communication between the flight crew and the cabin crew. At 1900, there was a strong odor noticed in the cabin by both the passengers and the cabin crew. Within a minute or so, the cabin crew recognized that there was a fire in the aft lavatory on the left side of the airplane. Multiple CO_2 fire extinguishers were deployed to arrest the fire in the lavatory. At 1902, the first officer attempted to view the aft lavatory, but was stopped by smoke midway through the airplane. By 1904:07, the first officer returned to the flight deck and informed the captain of the situation. Within seconds, the cabin appeared clear. By 1905, the captain asked the first officer to return to the aft lavatory using the captain's smoke goggles to get a first-hand appraisal of the situation. Within 30 seconds, the airplane electrical system showed anomalies to the captain. The first officer returned to the cockpit where the captain was attempting to diagnose the electrical system problems. By 1907:41, the master warning light illuminated. At 1908:12, the captain declared an emergency descent and asked for the nearest airport.

During the various attempts by the flight crew to understand the extent of the fire in the aft lavatory, the airplane had passed Standiford Field where the airplane could have landed. The airplane arrived on the ground at 1920:09 at Cincinnati International Airport. After this event, at least two specific changes and procedure reinforcements were made to respond to airplane fire events. First, all lavatories have smoke detection systems to alert crews of problems. Second, for any event where fire is suspected, flight and cabin crews must communicate immediately, and the flight crews will seek the nearest airport.



- Accident profile
  - June 2, 1983
  - DC-9
  - Cincinnati International Airport
- Fatalities: 23
  - 41 passengers
  - 5 crew
- Chain of events
- Changes
  - Smoke and fire detection system
  - New fire procedures

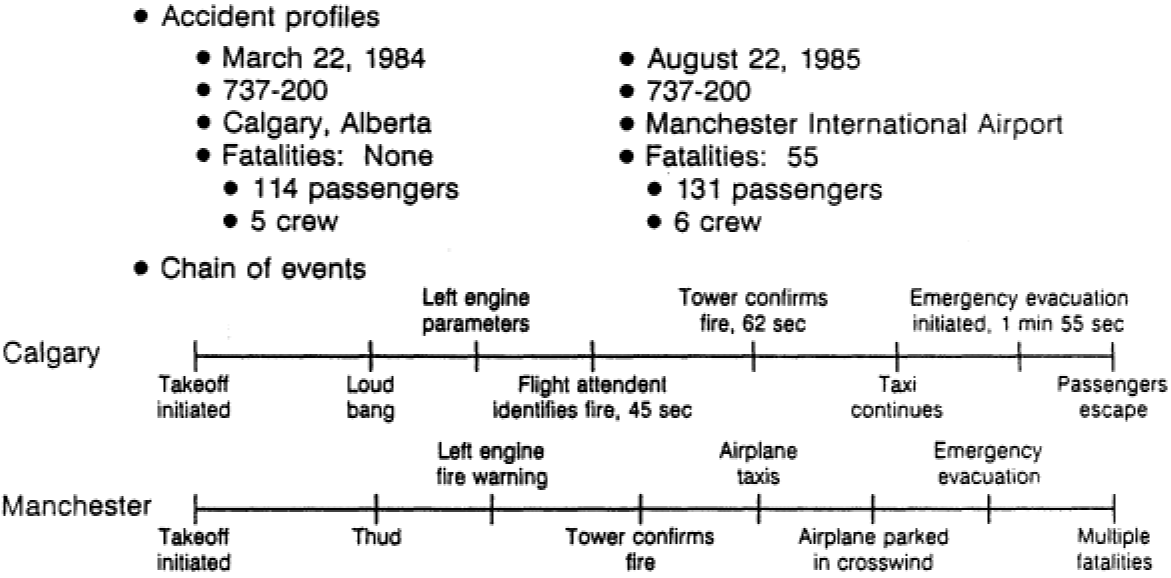
FIGURE 18 Lessons learned, DC-9 Cincinnati event. NOTE: Timelines not to scale.

Example: 737-200, Calgary and Manchester

The Calgary and Manchester events involving 737-200s were very similar; however, their outcomes were remarkably different (see Figure 19). In both events, the engine experienced an uncontained engine burst phenomenon. The wing fuel tanks were impacted. Fuel then spilled from the wing and ignited. The pilots, in both cases, were unaware of the extent of the fire. After becoming aware of the fire, the pilots chose to continue the taxi to exit the runway. Emergency evacuation was then initiated. However, the difference between the two accidents was the direction of the wind as related to the final stop for the airplane. For the Calgary case, the airplane was almost lined up with the wind. Thus, the fire did not penetrate the fuselage as quickly as in the Manchester case.

Some of the industry responses to these events included engine improvements (blade changes because of the Calgary accident and burner can improvements because of the

Manchester accident); fuel door improvements; reinforcement of known procedures for communications between the flight and cabin crews and for information flow from the tower to the flight crew; and reinforcement of current procedures by flight crews for fire events. One of the procedures that pilots were reminded of was the need to stop the airplane immediately. This action prompts airplane occupants to leave the airplane faster, promotes fuel runoff away from the airplane when fuel spills occur, and favors the wind direction.



- Accident profiles
  - March 22, 1984
  - 737-200
  - Calgary, Alberta
  - Fatalities: None
    - 114 passengers
    - 5 crew
  - August 22, 1985
  - 737-200
  - Manchester International Airport
  - Fatalities: 55
    - 131 passengers
    - 6 crew
- Chain of events

FIGURE 19 Lessons learned, 737 Calgary and Manchester events. NOTE: Timelines not to scale.

SUMMARY

Airplane fires, whether in-flight or on the ground, prompt not only apprehension in the flying public but also can cause major devastation, both to life and property. However, despite the enormity of the event, the commercial jet transport industry experiences such events very infrequently. Furthermore, most fire-related events are preceded by events where intervention at multiple points might prevent the accident.

Therefore, the commercial jet transport industry must retain its vigilance for preventing airplane accidents by examining accident event chains, understanding the various links in the chain, and then attacking multiple links to prevent the accidents.

Heat Exposure and Burning Behavior of Cabin Materials During an Aircraft Post-Crash Fuel Fire

*Constantine P. Sarkos**

ABSTRACT

The Federal Aviation Administration (FAA) has conducted numerous full-scale aircraft fire tests for the purpose of characterizing a post-crash cabin-fire environment and developing improved criteria for fire testing cabin materials. The tests subjected aircraft fuselages to an external fuel fire, usually adjacent to an opening in the fuselage. This paper reviews those tests. Emphasis is on the heating conditions experienced by the fuselage skin and cabin materials near an opening; the effect of wind and door openings on heat flux and cabin hazard development arising from the fuel fire; the important cabin phenomena related to survival, such as stratification of fire hazards and flashover; and hazard-time profiles and materials fire involvement.

BACKGROUND

Aircraft fire safety involves both in-flight and post-crash fire considerations. Fatal or uncontrollable in-flight fires are rare events; in fact, 30 years have passed since the last fatal accidental in-flight fire involving a U.S. commercial transport. Therefore, fire-test criteria for aircraft cabin materials, required by the FAA, are based primarily on post-crash fire conditions. Practically all post-crash aircraft fires are initiated by the ignition of jet fuel released from the damaged fuel system. Also, the relevancy of the fire performance of cabin materials to life safety is most relevant in survivable accidents when the fuselage is largely intact. Hence, an intact fuselage subjected to an external fuel fire represents a post-crash fire scenario in which burning cabin materials may affect occupant escape.

Past accidents, experimental studies, and a knowledge of fuselage design all show that a fuselage opening, perhaps a crash rupture or inadvertently opened emergency exit, provides the earliest opportunity for fire to enter the cabin. This mode of fire penetration contrasts with burnthrough of the fuselage shell. Burnthrough generally occurs later in time than when flame penetration occurs directly through an opening. In the past, the FAA has conducted many full-scale fire tests, utilizing the aforementioned scenario, which has an external fuel fire adjacent to an opening in an otherwise intact fuselage, to characterize post-crash cabin fires and to develop improved fire-test criteria for cabin materials. This paper reviews those past FAA full-scale fire tests.

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FULL-SCALE FIRE TESTS

Pool Fire

The heat flux created by a pool of burning jet fuel is dominated by intense thermal radiation. For pool fires greater than about 3 in. diameter, the radiative heat flux is relatively invariant and approximately 14 Btu/ft^{2}s (Eklund and Sarkos, 1980). The convective heat flux is roughly 10-20 percent of the radiative component, depending of the size of the fire and other factors, and is, consequently, of less importance.

Pool Fire/Fuselage Impact

One of the earliest experiments to measure the fuselage skin heating conditions arising from an adjacent fuel fire utilized a titanium fuselage (Sarkos, 1971). The test configuration was a 28-ft long titanium fuselage, 11 feet in diameter, abutting a 20-square-foot fire pit. The heat flux to the skin and flame temperature histories are shown in figures 1 and 2. During the test, a firewhirl developed adjacent to the fuselage at the aft end. At 80 seconds, the firewhirl unexpectedly moved to the forward end of the fuselage, where it lodged for 5-10 seconds, and then returned to the aft end, where it remained until the cessation of the test. The heat-flux measurements (total), which included the sum of the radiative and convective components, reflected the behavior of the firewhirl. When the effect of the firewhirl was minimal (center section), the heat flux fluctuated between 10 and 14 Btu/ft^{2}s, as expected. However, during the period of greatest intensification of the firewhirl, the heat flux attained peak values of 18 Btu/ft^{2}s. The flame plume temperature measurements closely followed the trends exhibited by the heat flux. Flame temperatures ranged from 1400-1800 °F when the effect of the firewhirl was minimal but increased to as high as 2000 °F in the firewhirl. The swirling motion of the firewhirl causes increased air entrainment, raising the air-to-fuel ratio and combustion efficiency. Although the titanium skin was an effective fire barrier, it is noteworthy that a cabin flash fire occurred at 2 minutes, caused by the ignition of combustible gases formed by the thermal degradation of the cabin pressure sealant elastomer, which was bonded to the interior of the titanium skin, and of the thermal/acoustical fiberglass insulation.

Radiant Heating of Cabin through Fuselage Opening

As discussed earlier, the creation of a post-crash fuel fire at a fuselage rupture or door opening provides the most immediate fire threat to the cabin interior. A series of experiments was conducted in which fuselage models under zero wind conditions were subjected to a fuel fire to determine the amount of radiation to the interior through a door opening (Eklund, 1978). The models were essentially empty cylinders lined with a ceramic fibrous insulation. Calorimeter measurements were taken at two locations: (1) on the fuselage symmetry plane, at an elevation of one-half of the doorway height, and (2) on the floor, midway between the doorway and symmetry plane. For external fuel fires, the heat flux measured at the symmetry plane and at the floor was 1.8 Btu/ft²s and 2.5 Btu/ft²s, respectively. This study also developed the equations for predicting the internal heat flux. The tests showed that the doorway could be treated as a black body radiating heat at a temperature of 1874 ° F. Figure 3 shows a representation of the heat flux to the interior calculated from the derived equations. It is evident that the high levels of radiative heat flux associated with the fuel fire will be confined to a small

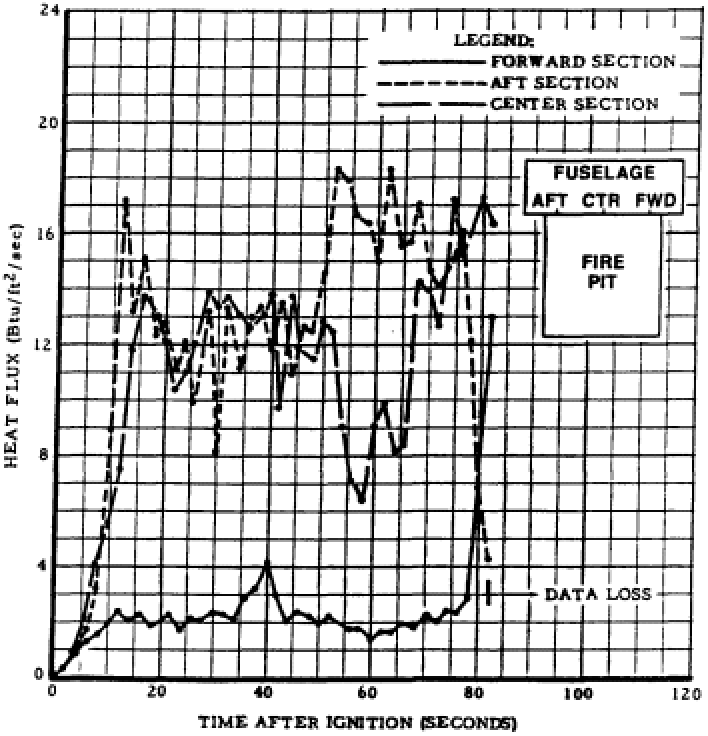
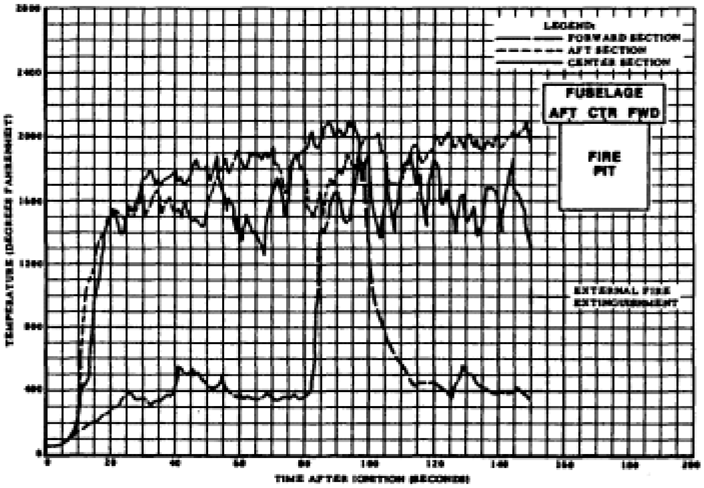


FIGURE 1 Titanium fuselage incident heat flux.



Time After Ignition (Seconds)
FIGURE 2 Titanium fuselage fuel-fire flame temperature.

region near the doorway when there is no penetration of the fuel-fire flames through the opening-for example, under a zero wind condition. Thus, during the early stages of a fire the thermal degradation and subsequent ignition of cabin interior materials will be very localized and limited to the doorway vicinity if the fuel-fire flames do not enter the cabin.

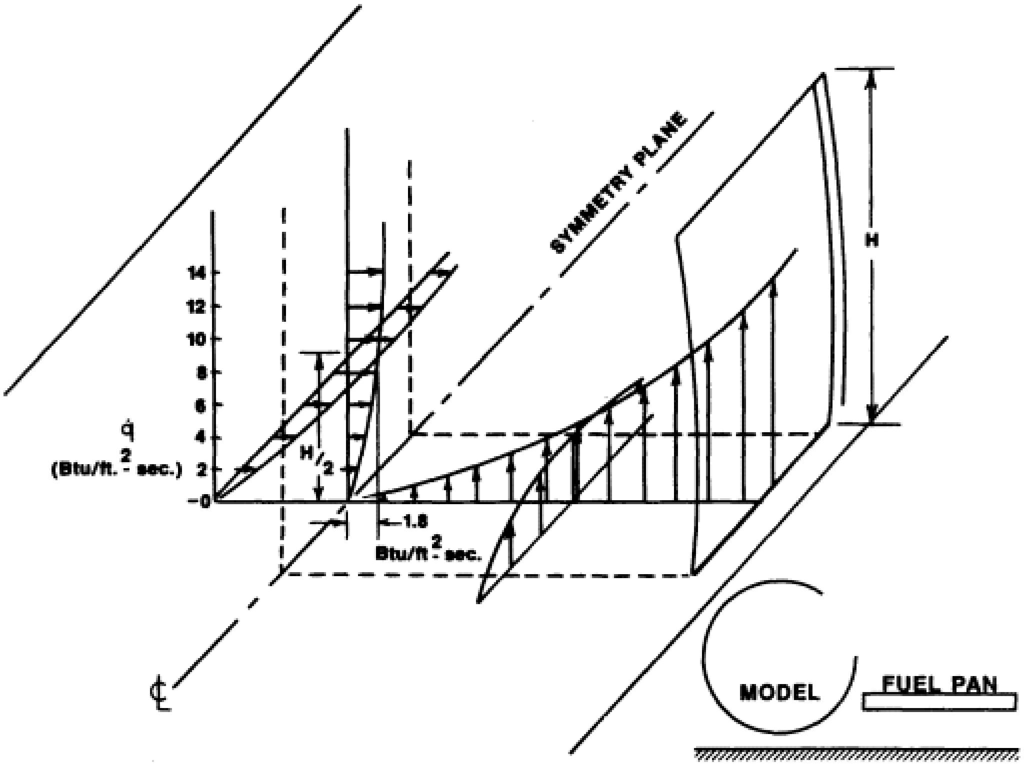


FIGURE 3 Theoretical radiative heat-flux profiles through a fuselage opening.

Effects of Wind on Cabin Heating

A series of full-scale fire tests essentially confirmed the modeling experiments discussed above (Brown, 1979). A fire-hardened DC-7 fuselage, protected on the outside with steel sheeting and lined inside with a ceramic fibrous insulation, was subjected to a 20-square-foot fuel fire. A doorway was placed alongside the fire, and two doorways were also placed away from the fire on opposite sides of the fuselage. The variation of the symmetry plane heat flux during three full-scale tests is shown in Figure 4. Conditions during the test with calm wind and all doors closed more closely matched the modeling experiments. In this case, the agreement between the modeling and full-scale results was very good. Test results suggested that when all doors were closed the pressure rise in the heated cabin, however slight, was not relieved and tended to prevent flame entry. In the test with all doors open and calm winds, the heat flux increased steadily above the modeling value. Higher heat-flux readings and significant variations were measured in the test with high winds (4-10 miles per hour) and all doors open. The fuel fire flames appeared to periodically enter and withdraw from the cabin, almost doubling the symmetry plane heat flux during peak heating conditions yet returning to the modeling value during minimal heating.

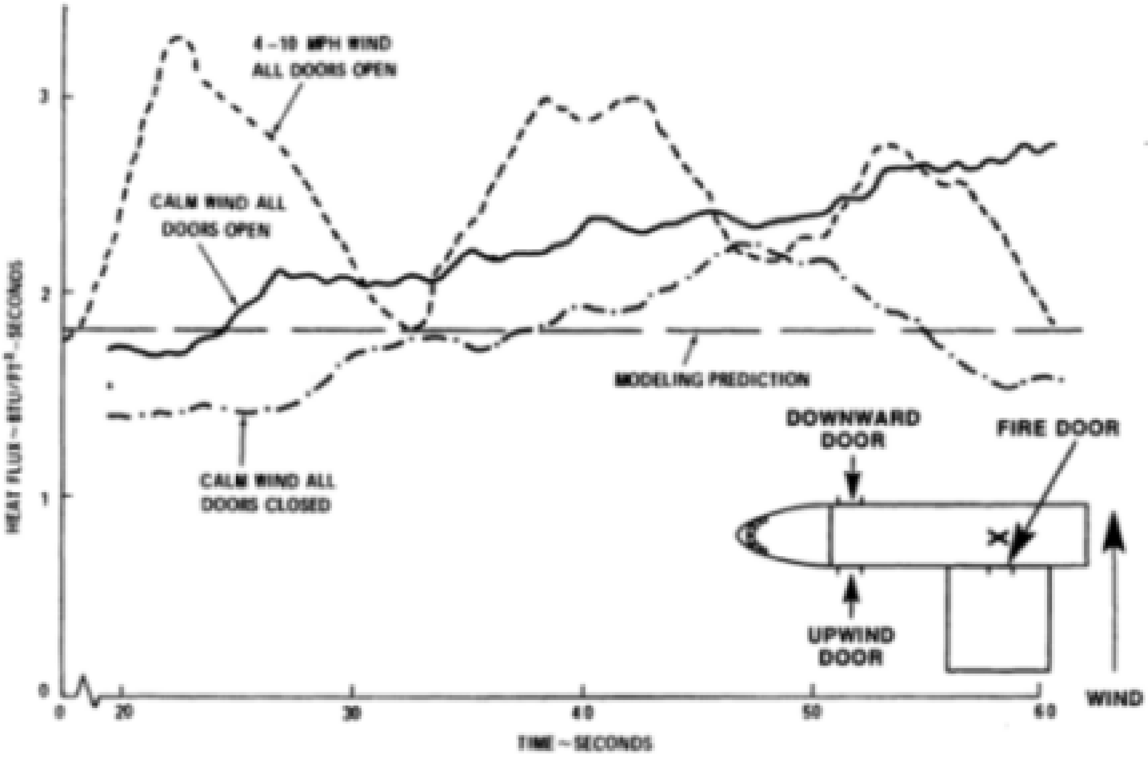


FIGURE 4 DC-7 symmetry plane heat flux.

Another factor that has been shown to have a critical effect on fire penetration is the door opening configuration. For the full-scale test conditions illustrated in Figure 5, the worst case is when the fuel fire is upwind of the fuselage and door openings are on the downwind side of the fuselage. In this case, the DC-7 tests have shown that there is a rapid development of fuel-fire hazards inside the fuselage. Conversely, if the door openings are on the upwind side only, the wind entering the door opening away from the fire has a buffering effect on fire penetration, and the accumulation of fuel-fire hazards within the fuselage will be greatly retarded. Figure 5 compares the ceiling heat-flux level for those extreme conditions. With minimal flame penetration, the ceiling heat-flux ranged from 1 to 2 Btu/ft²s. Current aircraft materials are virtually noncombustible under these heat-flux exposure values. Conversely, downwind door openings created maximum flame penetration, causing the ceiling heat flux to reach 10 Btu/ft²s. At this heat flux, aircraft materials will ignite quickly and burn rapidly. However, since the cabin became rapidly nonsurvivable from the fuel-fire hazards alone, the role of material flammability in cabin-fire hazard would be of minimal consequence in this scenario.

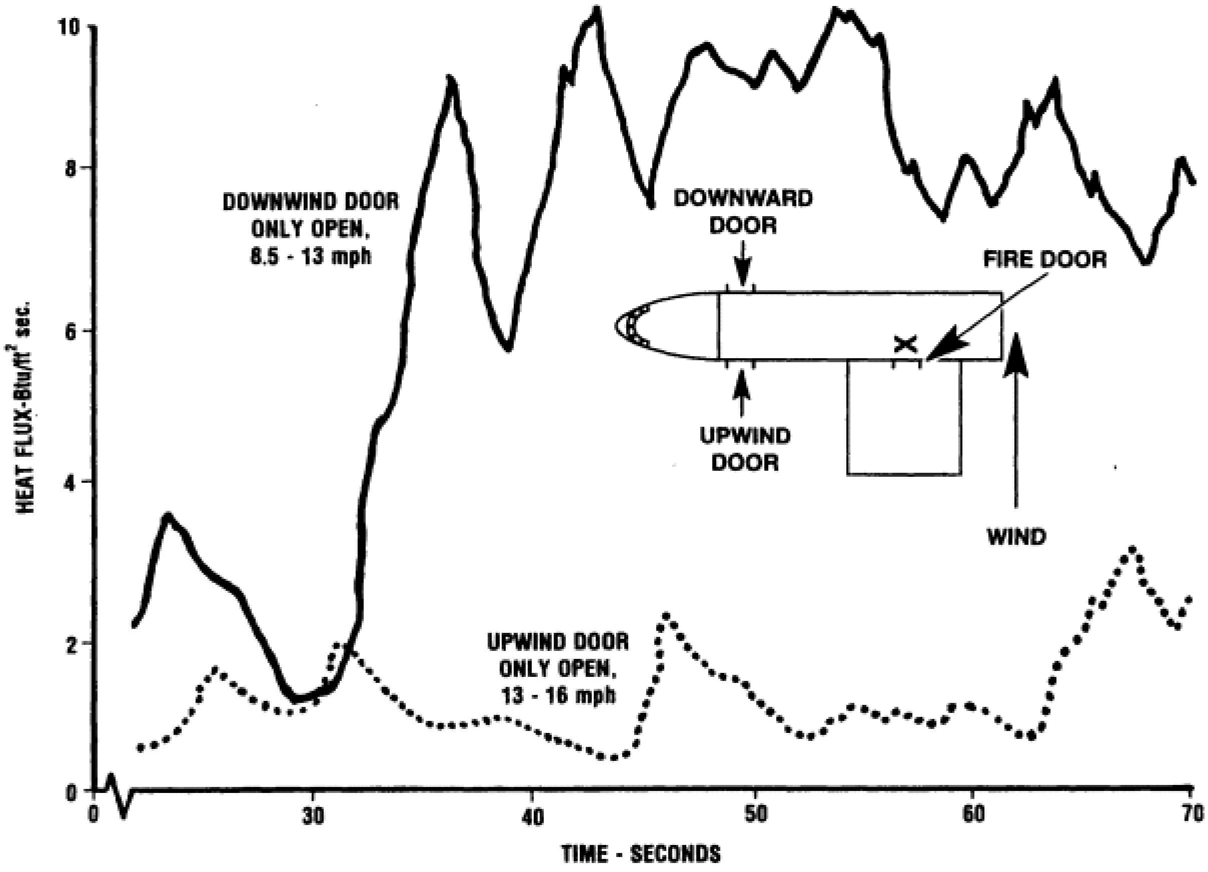


FIGURE 5 DC-7 ceiling heat-flux histories.

Fuel-Fire Hazards Accumulation within Cabin

In terms of the post-crash fire-heat exposure of cabin materials, the impact of fuel-fire penetration through a fuselage opening is twofold. First, materials in the vicinity of the opening will experience higher radiant heat exposure from fuel flames than when the fire does not penetrate, as discussed previously. Second, cabin materials will also be subjected to the hot fuel-fire smoke accumulating in the cabin. The quantity of hot smoke will increase as the flame penetration becomes greater. A large number of experiments were conducted in a wide-body (surplus C-133) test article, devoid of cabin materials, to examine the hazards associated with the fuel fire alone (Hill et al., 1979; Hill and Sarkos, 1980). An important finding was the pronounced stratification of heat, smoke, and toxic gases—that is, the hot smoke from the fuel fire accumulated at the ceiling. Results from a typical test are shown in Figure 6. The hot smoke layer near the ceiling was very distinct and did not thicken appreciably with time. Temperatures in the lower region were much lower than in the hot smoke layer and decreased almost linearly to near ambient conditions at the floor. Thus, heat exposure of cabin materials by a fuel fire adjacent to a fuselage opening consists of intense radiant exposure of materials very close to the opening and convective/radiative heating of materials in the upper cabin, including ceiling and stowage bins, extending over some area away from the fire penetration opening. The size of this area is determined by heat losses to the smoke layer due to mixing with entrained air and surface heat conduction. The heat losses are very substantial; for example, ceiling layer temperature gradients as high as 1000 °F along a 60-foot cabin length were measured during the C-133 tests.

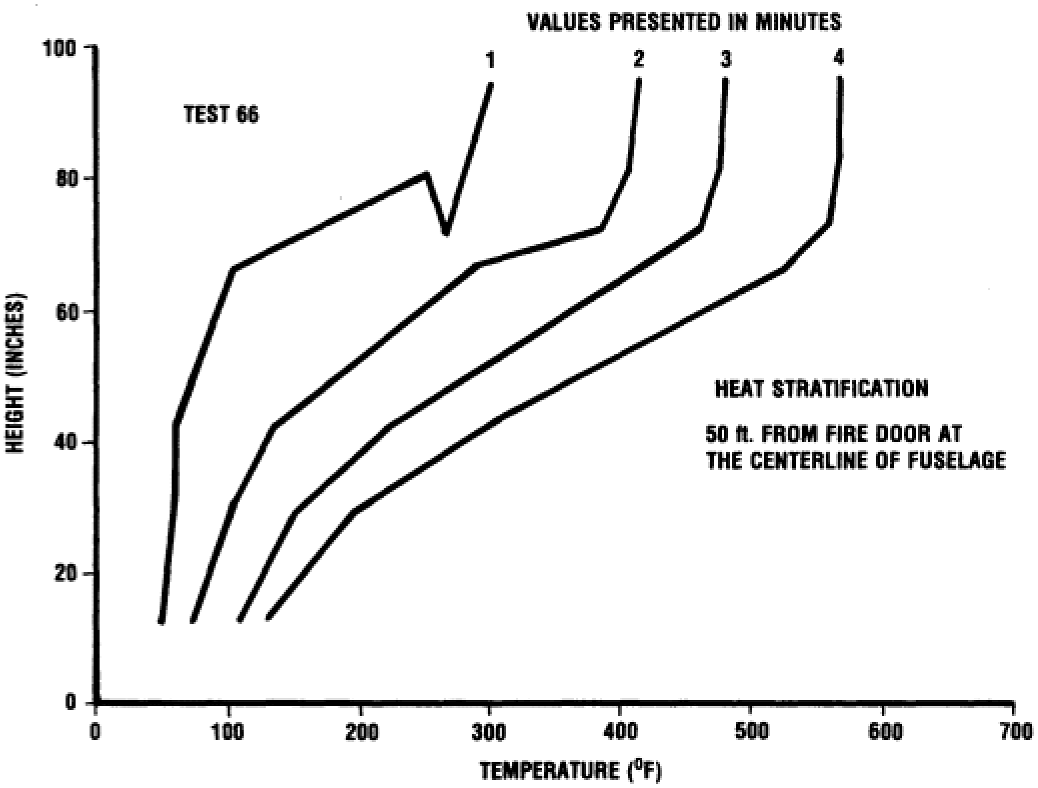


FIGURE 6 C-133 cabin air temperature stratification.

Characteristics of Burning Cabin Materials

The FAA has conducted numerous full-scale fire tests on cabin materials subjected to the previously discussed post-crash fire scenario, that is, an external fuel fire adjacent to a fuselage opening (Sarkos et al., 1982; Sarkos and Hill, 1982, 1985, 1989; Hill et al., 1984, 1985). The purpose of those tests was to determine survivability gains from improved materials and to develop improved fire-test criteria. Test observation and data analysis provide the following description of the characteristics of a cabin fire. The seat closest to the fuel fire is the initial material ignited. As the seat burns, its combustion products accumulate and spread along the ceiling. Later, the fire spreads to portions of the seats fore and aft of the initial seat ignited;

ceiling and stowage bins above the burning seats also ignite and burn. The fire remains localized and confined to the three outboard seats and overhead materials, which flash intermittently in the black smoke layer. A distinct partitioning of the cabin is created—a hot overhead smoke layer clinging to the ceiling, approximately 2 or more feet thick and a clear region below the smoke layer, largely at or near ambient conditions. The smoke layer spreads throughout the cabin. The observed fire below the smoke layer remains localized, and the two-zone effect persists until the occurrence of a flashover. Although definitions of flashover vary, it is basically a sudden, very rapid spread of fire within an enclosure. The extent of the spread of the fire is dependent on the availability of oxygen, which is consumed in great quantities because of the tremendous burning rates associated with the flashover.

Cabin flashover is clearly the critical factor affecting occupant survivability during a post-crash fire that is dominated by burning cabin materials (as opposed to a post-crash fire in which survival is governed by the fuel-fire hazards). Cabin hazard history measurements taken during a full-scale fire test in a wide-body test article are shown in Figure 7 (Sarkos and Hill, 1985).

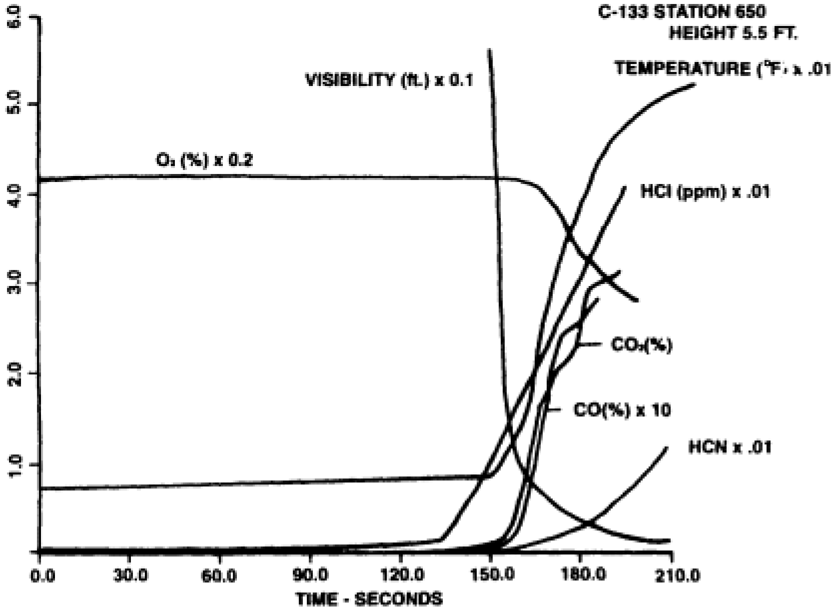


FIGURE 7 C-133 cabin hazard histories.

Before the flashover, which occurred at approximately 150 seconds, the cabin environment was clearly survivable; after flashover, the conditions deteriorated to such a degree that survival would have been highly unlikely. For example, as shown in Figure 7, within 30 seconds visibility was reduced from clear to 3 feet, temperature increased from ambient to 400 °F, carbon monoxide jumped from zero to 2,500 parts per million, and oxygen dropped from 21 percent to 16 percent. Obviously, improvements in post-crash fire survivability, when burning cabin materials predominate, can best be achieved by taking measures that delay the onset of flashover.

The primary areas of fire involvement during a post-crash cabin fire, as described above, are seats near the fire origin and ceiling materials. The most extensively furnished fire test in the C-133 wide-body test article corroborated this finding, which was observed in earlier experiments that employed a cluster of materials about the fire opening (Sarkos and Hill, 1989). In the "fully furnished" C-133 test, the forward cabin was completely furnished over a length of 45 feet (see experimental arrangement in Figure 8). Fourteen rows of seats, in a double-triple-double seating arrangement, and a triple seat in front of the galley (totaling 101 seats) were used. Aircraft ceiling panels, stowage bins, sidewalls, and carpeting were installed throughout the furnished cabin length, as well. As in previous experiments, survivability was driven by cabin flashover and extreme fire hazard gradients were documented. After the test, it was observed that the entire ceiling was consumed by fire, as were the outboard seats in the immediate vicinity of the fire door. On many of the remaining seats the dress cover of the seat back was largely burned away, but the seat fire-blocking material underneath was still present and intact.

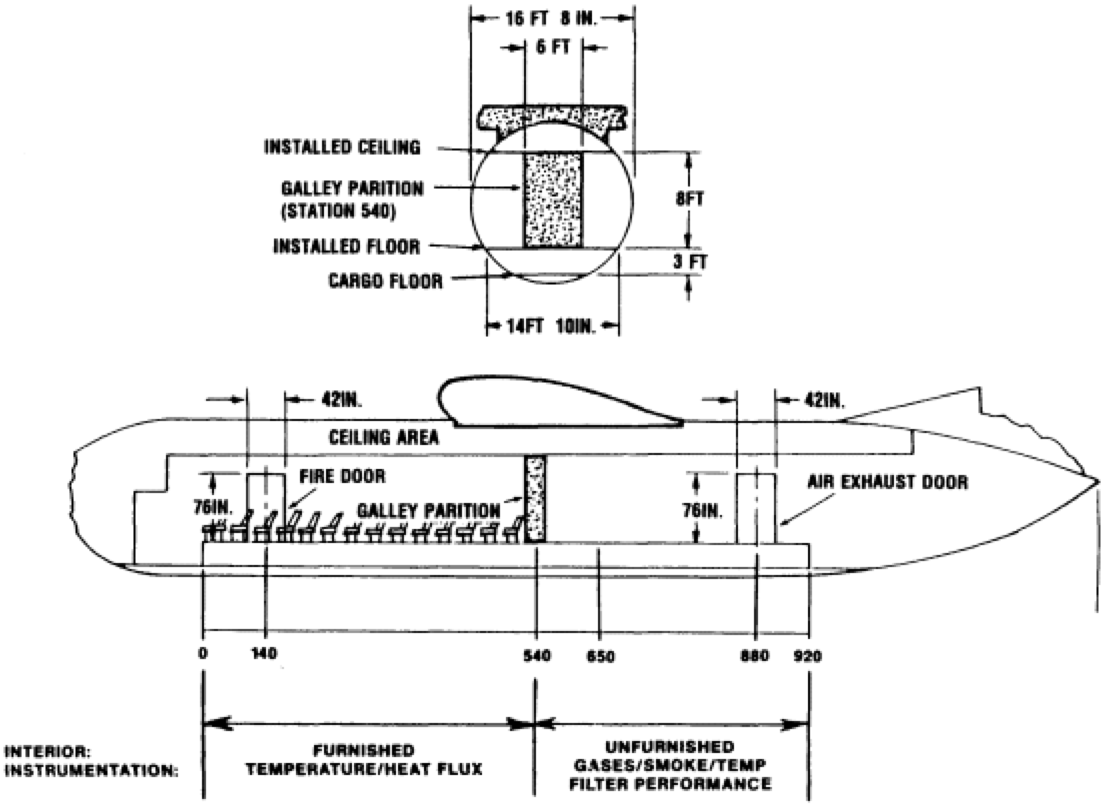


FIGURE 8 C-144 fully furnished full-scale test arrangement.

An account of the fire exposure/behavior of seats located away from the fire door is shown in figures 9 and 10. Thermocouples and calorimeter (facing the ceiling) measurements were taken near the top of the center seat at the noted seat rows (row 4 was at the fire door).

As shown in Figure 9, it appears that the onset of flashover occurred at 210 seconds. Before flashover, the data indicate that the fire had not spread to the center seats nor were these seats undergoing thermal degradation. After flashover, the seat top temperatures peaked at 1600 to 1900 °F. Based on the separation between the rising portions of the temperature profiles, the flashover propagated at a speed of approximately 60 feet/minute, or at a rate of one seat row about every 3 seconds. The trailing edge of the temperature profile shows the fire self-extinguished and the cabin cooled down. Oxygen concentration measurements indicated that the fire became oxygen-starved; oxygen concentration readings at the seat top level decreased to less than 5 percent throughout the test article. The calorimeter profiles in Figure 10 provide an indication of the duration and intensity of flaming combustion in the upper cabin caused by flashover. Total fire involvement of the upper cabin lasted for about 1 minute; the burning rate (heat release) was greater near the fire door and decreased toward the rear of the furnished cabin.

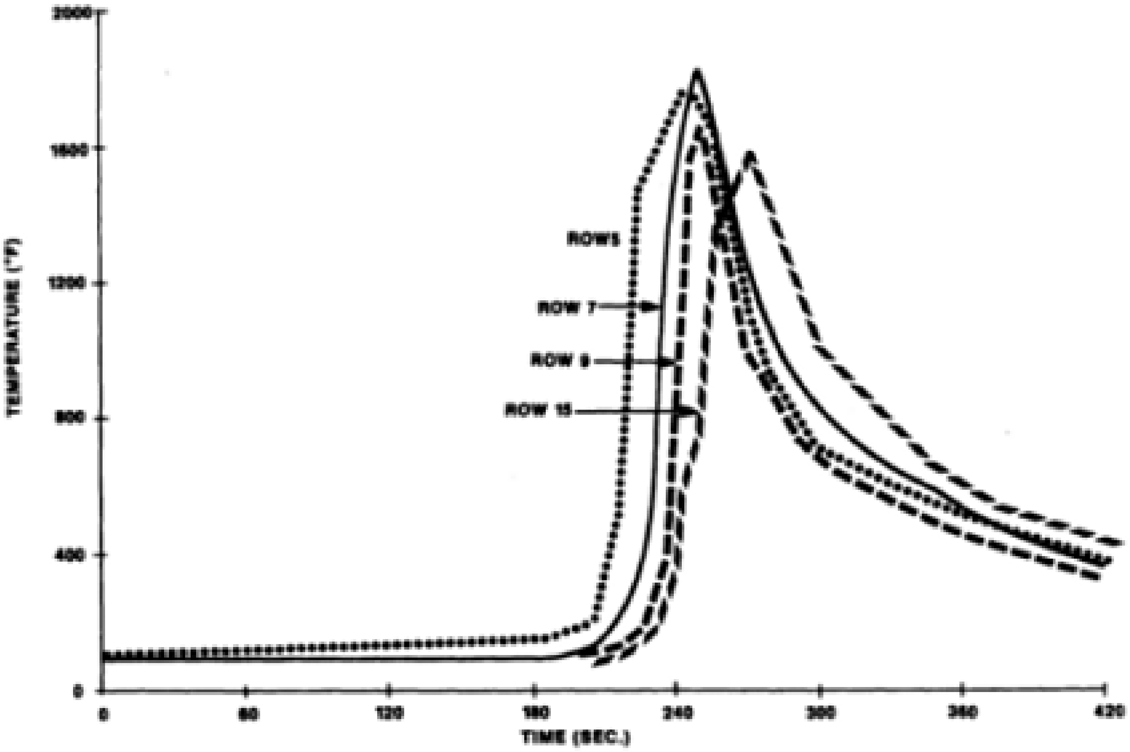


FIGURE 9 C-133 fully furnished test seat top temperatures.

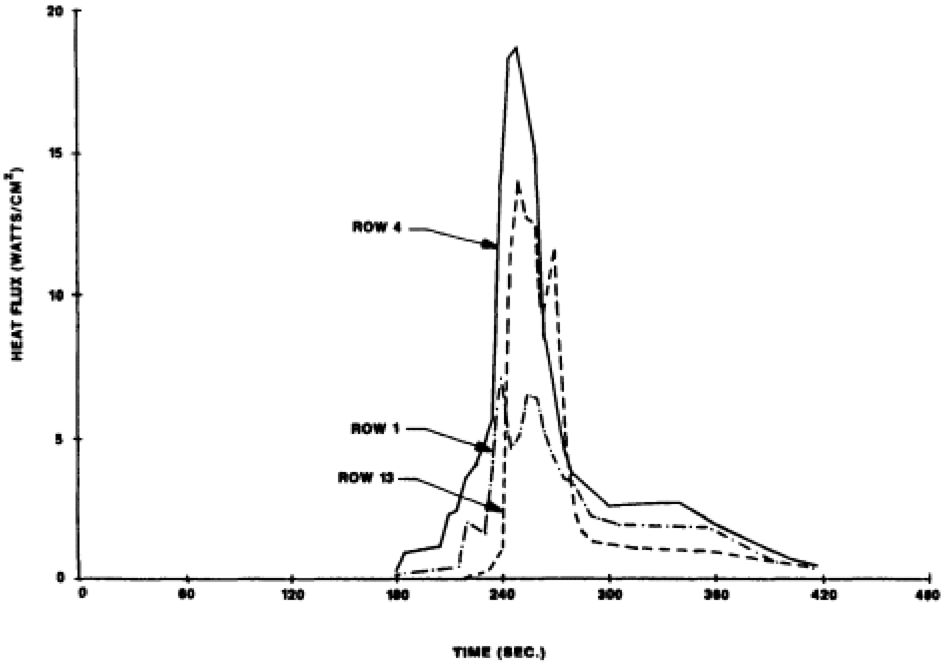


FIGURE 10 C-133 fully furnished test seat top heat flux.

DEVELOPMENT OF IMPROVED FIRE-TEST CRITERIA FOR CABIN MATERIALS

In recent years, the FAA has implemented two important standards to minimize the hazards of burning cabin materials during a post-crash fire (Sarkos, 1989). Full-scale fire tests have demonstrated that both material fire performance advances—seat cushion fire-blocking layers and low-heat-release panels—improve passenger survivability by extending the time of cabin flashover (Sarkos and Hill, 1982; Hill et al., 1985). Future development of advanced fire-resistant materials should aim to further delay or possibly eliminate the occurrence of flashover. The design scenario(s) should be based on a fuel fire that penetrates into the cabin through a fuselage opening but is not so severe as to cause nonsurvivable conditions from the fuel fire itself (without any involvement of cabin materials). Materials targeted for improvement should be initially focused on the upper cabin area (ceiling panels and stowage bins) and seat cushions and should be based on the measured cabin heating conditions and fire growth and the degree of material fire damage observed in full-scale fire tests.

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Fundamental Fire Properties of Combustible Materials

Dougal D. Drysdale[*]

ABSTRACT

The use of the term "fundamental fire property" in relation to a combustible material is misleading in that it suggests that measurements can be made of certain physico-chemical properties that determine unambiguously how that material will behave under fire conditions. This is true only to a very limited extent. In this paper, an attempt is made to clarify this issue and identify a number of fundamental properties that influence fire behavior.

INTRODUCTION

Combustible materials are widely used to improve the comfort and aesthetics of our surroundings not only in buildings but also in all modes of transport. In the aviation field particularly, there is a major advantage to be gained in that synthetic materials offer a considerable saving of weight over more conventional materials (particularly metals). However, the materials carry with them the risk that they may become involved in fire, rapidly creating conditions that will jeopardize the safety of the passengers. Control of the combustibility of these materials is necessary to minimize this particular hazard.

This is done conventionally by assessing the propensity of the materials to ignite and burn. Terms such as "ease of ignition," "rate of surface spread of flame," "rate of burning," and "smoke production potential" are frequently used as if they can be measured absolutely in tests such as ASTM E-84 (ASTM, 1981), but in fact the results of such tests are highly apparatus-dependent. The performance of different materials can be compared in a given test, and "ranked" accordingly; although this has provided the standard procedure by which materials are selected, it is based on a combination of experience and empiricism that has been shown to be deficient on a number of occasions.

The problem lies in the fact that "fire behavior" depends strongly on the fire environment to which the material is exposed. In principle, "fire behavior" can be quantified by examining the response of the material to the heat transfer associated with a specific fire scenario. In this context, "response" refers to the rate of surface temperature rise. For piloted ignition, the surface temperature must reach (or exceed) a critical minimum value (the firepoint) at which the rate of pyrolysis in the surface layer produces a flow of flammable vapors sufficient to support a flame (Figure 1). The time to ignition will depend on the net rate of heat transfer to the surface and the chemical and physical properties of the fuel. Similarly, once ignited, the maximum rate of burning (and the rate at which it will be achieved) will be strongly dependent

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on the heat-transfer environment—to which the burning fuel is now contributing. This is difficult to quantify, or control, which can explain many of the difficulties one encounters when attempting to interpret the results of standard test methods and apply them to "real fires."

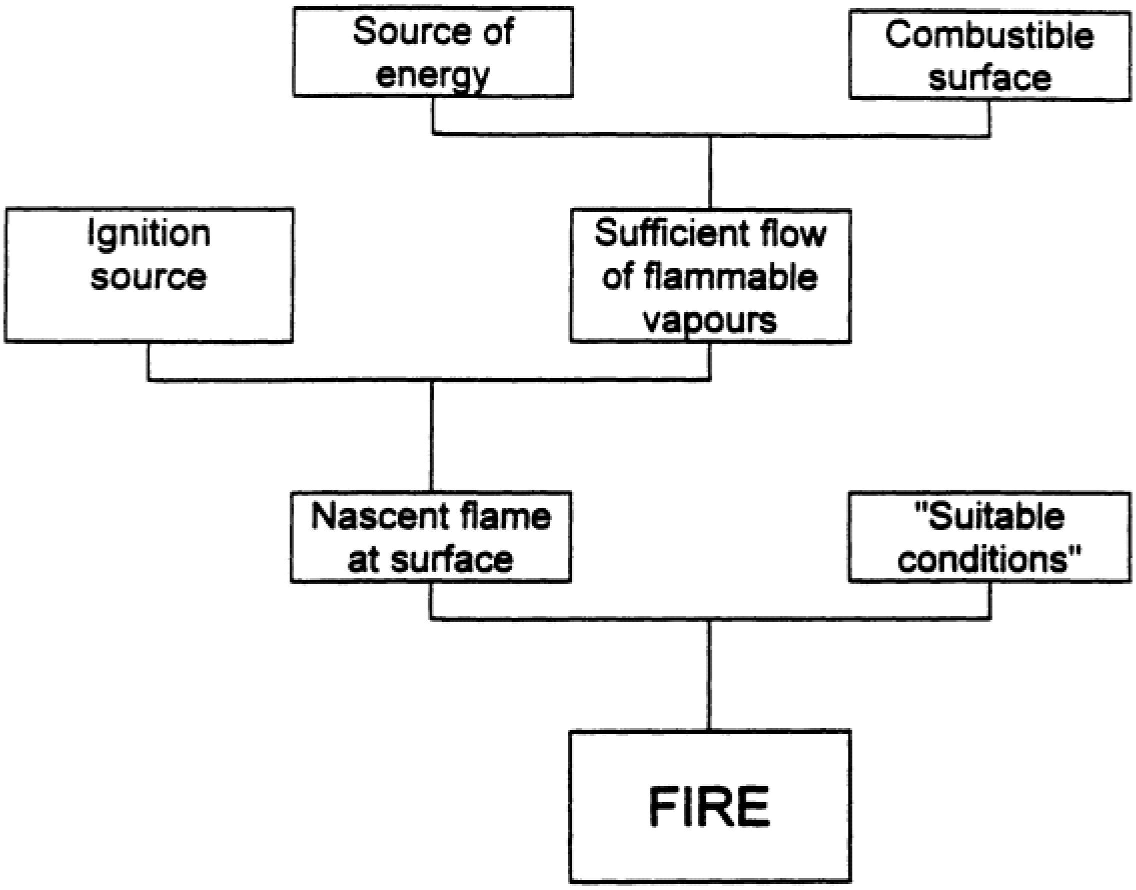

FIGURE 1 The scenario for piloted ignition.

THE BURNING PROCESS

It is appropriate to comment briefly on the burning process for a single, isolated "fuel bed." Following ignition, the surface temperature will increase rapidly as the developing flame provides additional heat transfer to the surface. The rate and extent of surface temperature rise will depend on the heat-transfer characteristics of the flame and other boundary conditions—in particular, those affecting heat losses from the fuel surface (see Equation 3 below; see also Drysdale, 1985). Heat losses will moderate the maximum rate of burning and can be critical in determining the acceptability of a material in a particular end-use situation.

FUNDAMENTAL PROPERTIES THAT INFLUENCE FIRE BEHAVIOR

Although it is extremely difficult to define a "fire scenario" adequately in terms of the heat transfer boundary conditions, it is possible to identify fundamental properties of a material which are important in determining how it will behave (or respond) under fire conditions. For convenience, these can be divided into physical and chemical properties.

Physical Properties

A wide variety of properties are important. These include the melting (or softening) point, thermal conductivity (k), density (ρ), and thermal capacity (c). However, physical form, shape, and orientation must also be considered. For composites, the possibility of delamination may be critical in some applications. The thickness of a material is of overriding importance if the material is "thermally thin" (i.e., the material heats uniformly when exposed to a heat flux, and there is no temperature difference between the front and the rear faces). In the case of piloted ignition, as represented by the scenario shown in Figure 1, simple heat-transfer theory shows that "thin" materials (thickness τ)are much easier to ignite (i.e., raise to the firepoint) than "thick" ones (Drysdale, 1985). For a material that is thermally thin, the time to ignition is given by the following expression: where *h* is the convective heat-transfer coefficient. Equation 1 shows that the greater the heat capacity of the material per unit surface area (ρcτ) the longer it will take to ignite. The derivation requires the assumption that there are no temperature gradients normal to the surface of the material (i.e., the temperature within the material is uniform at all times). The parameter that determines the rate of surface temperature rise for thermally thick materials is the thermal inertia (kρc) (Figure 2). Heat is conducted from the surface into the body of the material. This has a strong moderating influence on the rate of surface temperature rise if the material has a large thermal conductivity (such as steel). On the other hand, materials of low thermal inertia, such as standard polyurethane foam, are potentially very hazardous because the surface temperature rises rapidly when exposed to a heat flux. Similarly, a material with low thermal inertia will achieve its maximum rate of burning much more rapidly than one with a high thermal inertia. In general, combustible materials that are also good thermal insulators are potentially hazardous, unless they are intrinsically flame-retardant.

$$t_{ig} = \frac{\tau\rho c}{2h} \ln \frac{T_\infty - T_o}{T_\infty - T_i} \qquad (1)$$

If the melting point is less than the firepoint, the surface melt can flow away from the source of heat, rendering ignition more difficult, or even preventing it. In a test such as the Cone Calorimeter (ASTM, 1990) in which the sample under test is in a horizontal orientation, the consequences of the formation of molten polymer cannot be assessed. If the surface was vertical, the liquid would flow downwards, effectively removing heat from the exposed surface, perhaps giving a false impression in a small-scale test of how material may behave at full scale.

In a "real fire" situation, this can represent an additional hazard in that a liquid pool fire can form, with substantial risk of rapid fire spread as the liquid flows over the floor, thus increasing the area of burning and involving other combustibles.

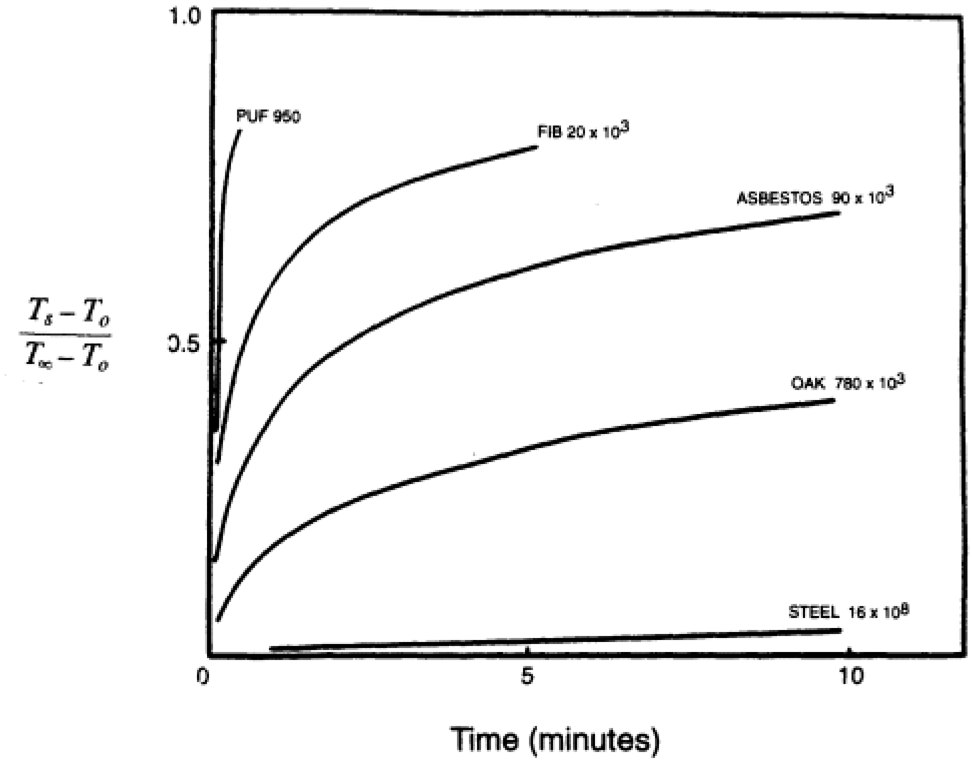

FIGURE 2 Effect of thermal inertia on the rate of temperature rise at the surface of a semi-infinite solid. FIB = fiber insulating board; PUF = polyurethane foam. The figures are values of ($k\rho c$) in W^2s/m^4 K. The calculation is for convective heat transfer to the surface, with h = 20 W/m²·K. T_s is the surface temperature, T_0 is the initial temperature of the solid, and $T_\infty$is the final temperature (Drysdale, 1985). Reprinted by permission of John Wiley & Sons, Ltd.

In general terms, materials that ignite easily will spread flame readily. The advancing flame front can be regarded as an advancing ignition front. However, the rate of spread is strongly influenced by the orientation of the surface and the direction of spread. Thus flame spread upwards on a vertical surface is much (as much as an order of magnitude) faster than horizontal spread over the same material. This is a function of the efficiency with which heat is transferred ahead of the burning zone. When flame is spreading vertically upwards, the material ahead of (i.e., above) the burning area is preheated as it is bathed by the flow of flame and hot combustion products. (In fact, caution is required with any sloping surface with an angle greater than about 20º, particularly if there is any degree of confinement; see Drysdale and Macmillan, 1992.)

Chemical Properties

Chemical factors of importance include the heat of combustion, the heat of gasification (equivalent to the latent heat of evaporation of a liquid), whether or not the fuel forms a char on heating, the firepoint temperature (the minimum surface temperature at which a self-sustaining flame can be established at the surface), the products of decomposition and combustion, the tendency of the fuel to form soot (hence smoke) when it is burning, and stoichiometry (in this context, mass of air required to burn a unit mass of fuel).

The firepoint temperature is determined by the kinetics and mechanism of the solid-phase decomposition process. In general terms, polymers with relatively high thermal stability (such as polyethylene) have a higher firepoint than those with low thermal stability (e.g., polyoxymethylene; see Thomson and Drysdale, 1987). If fire retardants are present, gas-phase inhibitors (such as HBr) may be released with the decomposition products, thereby reducing the *reactivity* of the fuel vapors and a higher rate of generation of the vapors is required before the firepoint is attained. In general, if these vapors are of "low reactivity," then the firepoint will be more difficult to attain.

Reactivity is a concept that does not lend itself readily to quantification. Rasbash has argued that measurement of the critical mass flux at the firepoint provides a means whereby reactivities of the vapors from different materials—and their flame retarded modifications—may be compared (Rasbash, 1975). The critical mass flux can be related to a critical value of the Spalding mass transfer number (Spalding, 1955), thus:

$$\dot{m}_{cr} = \frac{h}{c} \ln (1 + B_{cr}) \tag{2}$$

where *h* is the convective heat transfer coefficient appropriate to the heat losses from the flame to the surface; c is the heat capacity of air; and B_{cr} is given by $A/\square \Delta H_c$ where A = 3,000kJ/g; ΔH_c is the heat of combustion of the vapors; and φ is the maximum fraction of the heat of combustion of the vapors that the flame can lose to the surface by convection. φ can be taken as a measure of the "reactivity" of the vapors, but the evaluation of φ requires a reliable value of *h* that is very sensitive to the experimental configuration.

This approach has not been investigated in great detail, although the principle has been clearly demonstrated (Thomson and Drysdale, 1989). Data on properties relating to the evolved vapors (e.g., their heat of evolution, heat of combustion, and reactivity) could provide a more fundamental method of assessing combustible materials, which in turn could help in formulating strategies for research to investigate "new" materials.

Firepoint temperature is more easily measured than the critical flow rate of the vapors (Thomson and Drysdale, 1987) but cannot be used on its own as a means of selecting a material (except under rare conditions where there is strict control over potential ignition sources). A higher firepoint may easily be offset by unfavorable thermal properties, such as a low thermal inertia. In any event, post-ignition behavior must be taken into account in any hazard assessment. A degree of resistance to ignition may be achieved at the expense of an increase in the yield of smoke and toxic gases. This is not uncommon, as many fire retardants act by inhibiting the combustion process that will increase the yields of partially burned fire products.

Although the heat of combustion is obviously significant, it is the rate at which heat is released that is the more important parameter. Indeed, it has been argued that the rate of heat release (RHR) is the most important parameter in determining fire hazard (Babrauskas and Peacock, 1992). The Cone Calorimeter was designed to allow RHR to be measured under a range of imposed heat fluxes up to 100 kW/m². As implied above, RHR is not a material property per se, as it depends on the heat-transfer boundary conditions at the surface that are strongly scenario-dependent. The rate of burning can be expressed as a rate of mass loss: where the burning rate is expressed as a mass flux of fuel vapor from the surface; $\dot{Q}''_{flame}$ is the heat flux from the flame to the surface; $\dot{Q}''_{ext}$ is the heat flux from any external source (e.g., flames under a ceiling, or the conical heater in the Cone Calorimeter); $\dot{Q}''_{loss}$ represents the heat losses from the surface, expressed as a heat flux through the surface, and L_v is the heat of gasification. (Flammable liquids have much lower values of L_v than solids, as there is no chemical decomposition involved in releasing the vapors; consequently, they burn very much more rapidly.) In principle, the RHR can be calculated from the product of $\dot{m}''$ and the heat of combustion, with an appropriate correction factor for incompleteness of combustion. This equation shows clearly that RHR cannot be considered in isolation from the "fire scenario."

$$\dot{m}'' = \frac{\dot{Q}''_{flame} + \dot{Q}''_{ext} - \dot{Q}''_{loss}}{L_v} \qquad (3)$$

Fuels that form a char have the advantage that at an early stage a barrier is formed at the surface, which insulates the unaffected material underneath. Heat then has to be conducted through the char. This is one reason for the remarkable properties that wood has under fire conditions. The formation of char indicates that some of the fuel remains behind and does not burn as a flame. It may burn subsequently as a smoldering process but at a greatly reduced rate of heat release.

Fire products consist mainly of carbon dioxide and water vapor, but the few percent of partially burned products have the potential to cause considerable harm. Smoke results in loss of visibility, which delays escape and can lead to unacceptable exposure times for those attempting to evacuate a building. The tendency of a fuel to produce smoke can be assessed by means of a single measurement (the "smoke point"; de Ris, 1994, but "ranking" materials in one of the standard tests (e.g., ASTM E-1354 [ASTM, 1990] or ASTM E-662 [ASTM, 1983]) can be misleading. Little attention has been paid to the question of whether a "smoke test" is desirable, given the fact that the yield of smoke from a given material in a real fire is highly dependent on the fire scenario, including the ventilation to the fire. Indeed, smoke yield changes as a fire progresses through the early stages to flashover and beyond. All "smoke tests" are well-ventilated and are therefore relevant to the early, pre-flashover fire. The problem is in the fire process itself, in that a fuel may have a certain measurable propensity to produce soot/smoke, but the inefficient combustion that will inevitably occur in a real fire will alter this in a manner that cannot readily be predicted.

The same comment is equally applicable to the assessment of the production of toxic and corrosive gases in fires. Present experimental methods of assessment are poorly understood and cannot be assumed to be helpful. It seems that the "propensity to produce smoke and toxic gases" is even more scenario-dependent than the other "fire properties" that have been discussed above.

CONCLUSION

It is possible to identify a number of measurable properties of combustible materials that provide an understanding of their behavior in fires. However, the so-called "fire properties" (ignitability, rate of surface spread of flame, etc.) are scenario-dependent. They can be properly assessed only if the characteristics of the scenario are taken into account.

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Fire Tests and Hazard Evaluation

James G. Quintiere[*]

INTRODUCTION

The objective of this paper is to discuss the process of using fire tests to evaluate the potential fire hazard of materials and products. The accuracy of this process bears on the integrity of fire safety practices and on fairness in the marketplace. The evaluation process must be consistent with the fire scenario of concern. Consideration needs to be given to the configuration of the product or material, the configuration of its environment, and the elements at risk. This paper emphasizes the hazards associated with the combustion of materials and products and, in particular, "flammability" testing.

Flammability tests have traditionally been stylized tests that give measurable impressions of the fire growth process on a material or product. Generally, they lead to rankings and class categories for materials that control their use through regulations. These methods lack universality and tend to differ from one region to another. They have provided an empirical basis for fire safety regulation that is generally acceptable. However, periodically they are surprised by new products or their applications, and the safety measure they sought is unsuccessful. Moreover, these test results and data do not provide any basis for engineering analysis. Indeed, their basis is only weakly supported by scientific principles at best.

Scientific methods have been developed in the field of fire that offer some alternative to the traditional approach to flammability. This approach is based on material fire property data and on scientific calculations. Unfortunately, fire scenarios are complex and our knowledge is too immature to provide a complete basis for this approach. However, its continued evolution and its technical merits make it an attractive alternative to the current state of material flammability testing.

In general, the process of evaluating the fire safety of materials and products should maintain the following attributes:

- material and product representation,
- scenario representation,
- scientific foundation, and
- sensitivity to scenario variables.

The last attribute is introduced because fire growth tends to be exponential in character, and changes in scenario variables can lead to significant differences in fire growth. This form of surprise is unacceptable.

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This paper addresses the status of material fire hazard assessment, the factors that need to be considered, and the status of scientific understanding.

HAZARDS DUE TO FIRE

Hazards due to fire depend on the elements at risk. These elements might include people, goods or equipment, and the global environment. Hazards to people consist of the following:

1. thermal hazards due to temperature, which may cause burns;
2. obscuration due to smoke, which may cause loss of sight; and
3. toxicity due to products of combustion, which may cause biological dysfunctions.

Hazards to goods or equipment may be thermal destruction, fouling, or corrosivity. Hazards to the environment may be considered as chemical or thermal pollution effects. The tolerance to each hazard must be quantitatively known and assessed against appropriate measures of hazard from the fire test of a material. In this paper, the relationship is examined principally for the fire hazards associated with people.

MEASURES OF HAZARD

The measures of fire hazard associated with people are represented by the following quantities:

- temperature (T),
- combustion product concentration (X_i), and
- smoke visibility (L_v).

Time exposures to temperature and gas concentrations give an extent of damage and hazard. Various relationships exist to make these assessments. For example, according to Purser (1988) lethal conditions for a person engaged in light activity from exposure to carbon monoxide (CO) are approximately given by where *t* is the exposure time. (Note: 1,000 ppm = 0.1%.) Visibility influences time to escape the effects of the fire.

$$X_{co}(\text{ppm})\, t(\text{min}) = 0.72 \times 10^5 \qquad (1)$$

The measures of hazards (T_i, X_i, L_v) are "intensive" variables of the fire that vary spatially and in time. They primarily depend on the fire growth or burning rate ($\dot{m}$) and on the material properties. In addition to flow and geometric conditions, these functional relationships can be represented as where the burning rate is multiplied by the material properties: ΔH_c the heat of combustion, X_i, the yield of combustion product *i* per mass of material; and D_m, the mass optical density of the material. The mass optical density is basically the attenuation coefficient ($\dot{m}^{-1}$) divided by the decomposed mass per unit volume of combustion products (g/m^3; see Quintiere, 1992). The main point of Equation 2 is that the "extensive" fire variable, $\dot{m}$, and the material properties control the hazard variables, T, X_i and, L_v. These material properties are measurable and have been extensively documented by Tewarson (1988) and others. They form a basis for the computation of the hazard variables provided $\dot{m}$ can be determined.

$$T = f_T(\dot{m}\,\Delta H_c) \tag{2a}$$

$$X_i = f_i(\dot{m}\,\gamma_i) \text{ and} \tag{2b}$$

$$L_v = f_v(\dot{m}\,D_m) \tag{2c}$$

As an example, some typical values for these material properties are listed in Table 1 for generic materials. These are based on data from Tewarson (1988) and a study on furniture flammability that utilized such data (Quintiere, 1990). These properties can change significantly as the fire conditions become fuel-rich. This is the "ventilation-limited" condition in a compartment fire when less than stoichiometric air is supplied. For example, γ_{co} can attain 0.14 for wood under these conditions (Tewarson, 1988). Also, under fuel-rich conditions, incomplete combustion will cause greater yields of soot and intermediate hydrocarbon species. Thus, D_m would increase and ΔH_c may decrease. Under ventilation-limited conditions, the resulting fire hazards may be more attributable to the fire conditions than to the fire growth on the product or material that promoted the fire condition. For this reason, the phenomenon of "flashover" in compartment fires needs to be considered as a distinct hazard event that can result in a ventilation-limited fire state.

TABLE 1 Typical Material Properties

Material	ΔH_c (kJ/g)	γ_{co}(g/g)	D_m(m^2/g)
Wood	12	0.004	0.04
Plastic	27	0.06	0.3
Fire Retarded	7	0.05	0.3

FLASHOVER AND VENTILATION-LIMITED FIRES

The phenomenon of flashover is an event that can be described as the transition in a compartment fire from the development of a fire in a distinct location of the compartment to the full involvement of the compartment in the fire. It can be manifested by preheating the uninvolved combustibles to their ignition temperatures or by fuel gas-phase and air-flow processes. The onset of this transition to full involvement is usually sudden and unexpected, and it can take less than a minute to occur. Figure 1 illustrates a typical evolution of a compartment fire to flashover—in this case, a ventilation-limited fire. The measurements displayed are indicative of the products of combustion from this furnished room fire (12 feet x 18 feet x 8 feet high) initiated by smoldering on an upholstered chair. Flashover is indicated after 25 minutes with the fire moving to full involvement of the room contents. The reduction of oxygen concentration to zero following flashover is indicative of the ventilation-limited state.

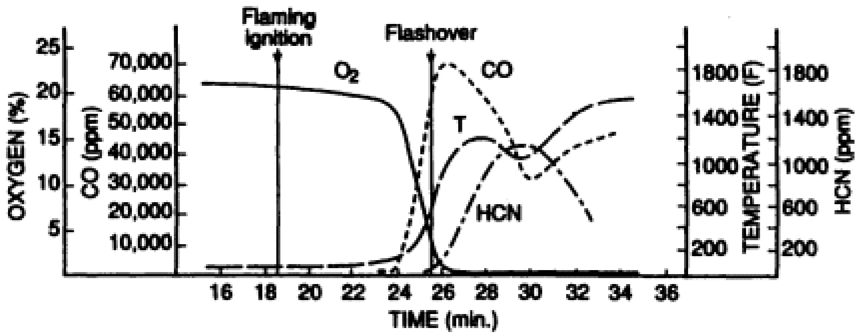

FIGURE 1 Illustration of a flashover in a furnished room fire (Belles, 1985). Reprinted with permission from D.W. Belles, *NFPA Journal*® (Vol. 79, No. 2), Copyright© 1985, National Fire Protection Association. *NFPA Journal*® is a registered trademark of the National Fire Protection Association, Inc., Quincy, MA 02269.

The event of flashover is a serious hazard consideration because the subsequent growth of the fire is now controlled by the extreme thermal conditions of full involvement. The burning rate is dramatically increased, and many items are involved. Also, the production of soot and carbon monoxide become a serious problem to people remote from the fire. However, evidence in some recent high-rise building fires involving several floors showed that occupants above the fire were not subject to lethal levels of carbon monoxide if the floor fires were not ventilation limited. Hence, high-rise structures with large window areas that break in a fire could be beneficial.

An illustration of the range of possible conditions that can result in a typical residential room fire is shown in Figure 2. This analysis was based on data from Table 1 (Quintiere, 1990). It shows three critical stages of a compartment fire.

Development Fire

During this "development stage," the fire is controlled by the fire growth on the material or product. The effect of the compartment on the fire is relatively significant. When the flames reach the ceiling, more-significant compartment heating occurs. At this point, the fire is still well-ventilated, and the equivalence ratio (φ; i.e., the ratio of fuel to air supply relative to stoichiometric fuel to air) is estimated in Figure 2 as 0.1. Smoke obscuration can be a problem during this stage, but carbon monoxide would not be a serious concern according to Equation 1.

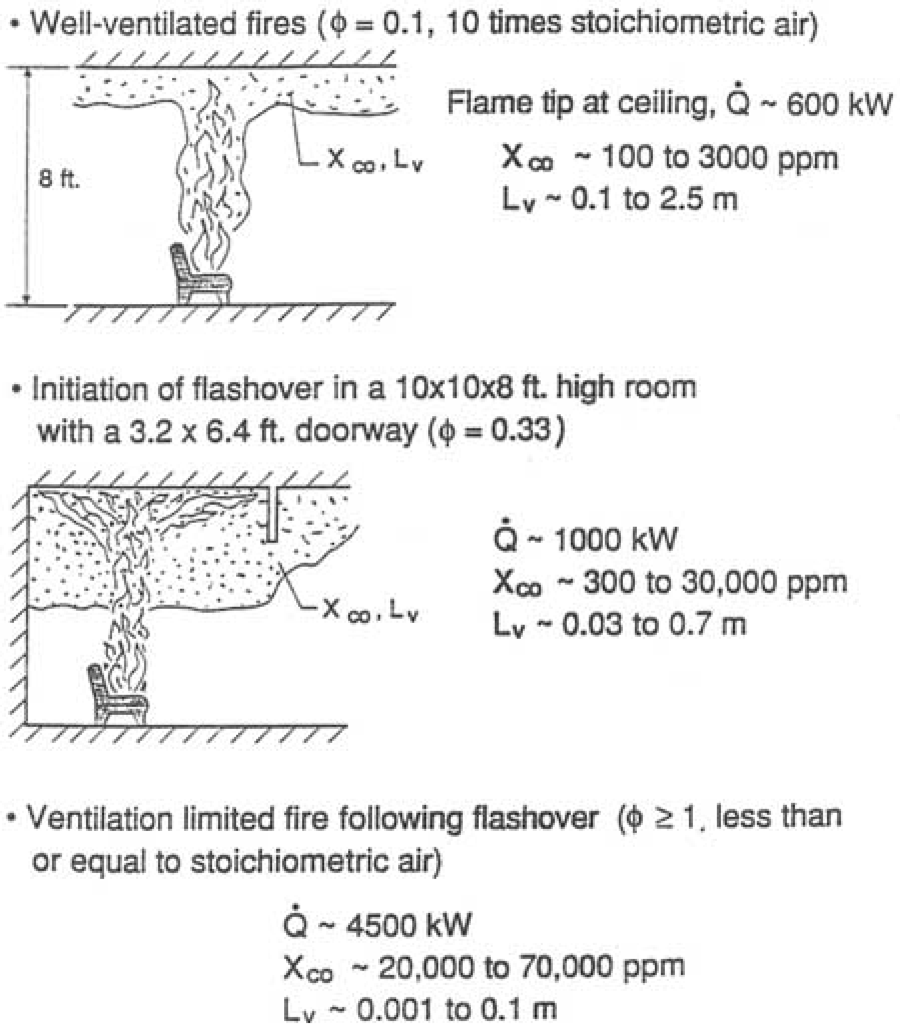

FIGURE 2 Range of possible conditions in a typical residential room fire (Quintiere, 1990).

Onset of Flashover

The initiation of flashover was assumed at a compartment gas temperature rise of 500 °C. At this point, the fire is still well-ventilated with three times stoichiometric air. From hazard estimates, it can be seen that some materials can pose serious hazard conditions, but the occurrence of flashover would make conditions much worse. Thus, flashover also marks a transition from a fire state that is controlled by material fire growth to a state of elevated temperature in which many more materials and products contribute.

Ventilation-Limited Fire

For typical residential rooms, the contents and ventilation openings usually lead to the ventilation-limited fire state following flashover. Most combustible contents become involved, and the incomplete combustion state in the room leads to flame extensions to the surroundings and to greater burning rates and yields of soot and toxic products, such as carbon monoxide.

THE DEVELOPING FIRE ON MATERIALS AND PRODUCTS

The evaluation of the fire hazard due to materials and products must depend on the fire scenario. The role of the regulator and the engineer is to define the scenario at issue. In most regulatory applications, the concern is the early development of a fire on a material or product due to a plausible ignition source. This process would comprise the developing stage of the fire and would principally be a result of the material properties. Whether flashover is considered as the critical condition for hazard, or tolerance levels associated with the variables T, X_i, and L_v, a primary measure of hazard is the burning rate, $\dot{m}$, Equation 2. Moreover, if the thermal hazard is perceived as the most significant hazard during this period, then the energy release rate, $\dot{m}\Delta H_c$ is the key hazard indicator. This is the underlying premise for most "flammability" tests for materials and products. However, the concept of flammability is complex, being composed of several distinct processes.

FLAMMABILITY COMPONENTS

Material flammability is defined as the process of fire growth on the material due to ignition and the resulting release of energy. It is composed of the following processes:

1. ignition,
2. flame spread, and
3. burning rate.

Mathematically, this can be represented by the energy release rate following an ignition challenge:

$$\dot{Q} = \dot{m}\,\Delta H_c \text{ and} \tag{3}$$

$$\dot{m} = \dot{m}''\,A \tag{4}$$

where $\dot{m}''$ is the burning rate per unit area, and A is the area involved due to flame spread. Each of these components are distinct phenomena that do not necessarily depend on the same factors.

Dependent Factors

The components that represent flammability can be examined further in view of the state of current knowledge in order to describe their significant dependent factors. More-detailed descriptions can be found in the literature on fire growth (e.g., Quintiere, 1992). Here, the more important factors are qualitatively listed below.

Ignition

Time to ignite depends on:

1. ignition temperature,
2. thermal properties, and
3. ignition heat flux.

Flame Spread

Lateral or horizontal flame spread rate depends on:

1. ignition temperature,
2. thermal properties, and
3. flame heat flux.

Upward or ceiling flame spread rate depends on:

1. ignition temperature,
2. thermal properties,
3. flame heat flux, and
4. flame length (which is dependent or energy release rate).

Burning Rate

Burning rate per unit area depends on:

1. thermal and decomposition properties,
2. flame heat flux, and
3. time.

In examining these factors, it is seen that some are identical. Flame heat flux that depends on orientation is a factor of considerable prominence and is not necessarily the same for each flammability component. Time is a factor in all cases, with upward flame spread rate possibly being exponential in time. Time is explicitly listed under burning rate to symbolize that the process is not steady and that the burning time is a significant factor in flammability. It is probably seen more clearly from these dependent factors that these components of flammability are independent although they are integrated in the process of fire growth. Any attempt to evaluate the flammability hazard from these components, or from stylized test methods, must be consistent with the fire scenario of concern, or there will be differences in the perception of hazard.

FLAMMABILITY HAZARD CLASSIFICATION

Wall and ceiling products for building construction have been extensively regulated with respect to fire safety. Many flammability test methods address this situation. Due to lack of confidence in such tests and as a basis of validation, full-scale standard room tests have been developed for these configurations. Several "room-corner tests" exist with various corner ignition procedures. For example, the International Standards Organization (ISO) Room-Corner Test subjects the wall and ceiling material to an ignition source of 100 kW for 10 minutes followed by 300 kW for additional 10 minutes if flashover (1,000 kW) has not yet been reached. Extensive tests of materials in the ISO scenario have been described by Sundström (1986) and Söderbom (1991). Additional data, for these same materials, have been taken in European national tests and in new tests such as the Cone Calorimeter. These data have provided a basis for analysis and evaluation of methodologies. Many of these studies have contributed to the process of selecting a unified flammability test for the European Community. That process has not yet been successful and has identified the deficiencies with the current national tests. The lack of harmony represents the general status of identifying a universal flammability hazard methodology for this important problem.

Classification by Traditional Tests

An example of the status of national test methods to rank the performance of wall and ceiling materials in the ISO Room-Corner Test is shown in Figure 3. These results are based on a compilation by Sundström and Göransson (1988). They classify the performance in the ISO Room-Corner Test for 13 materials according to the time to flashover or energy release rate into five classes plus an unclassified category (UC) for the worst materials. Results from the national tests of England (0-4), Germany (Al, 2, B1-3), France (M1-M4), Holland (1-4), and Sweden (I-III, UC) were also included. To present those results in a unified graph, only four classes were considered for each classification system. The ISO Room-Corner Test is represented as no flashover in Class 1, and decreasing flashover times with the most rapid flashover (~ 1 min) in Class 4. National tests with five categories were classed into four, for example, England 0 = Class 1, and Germany A1 and A2 = Class 1.

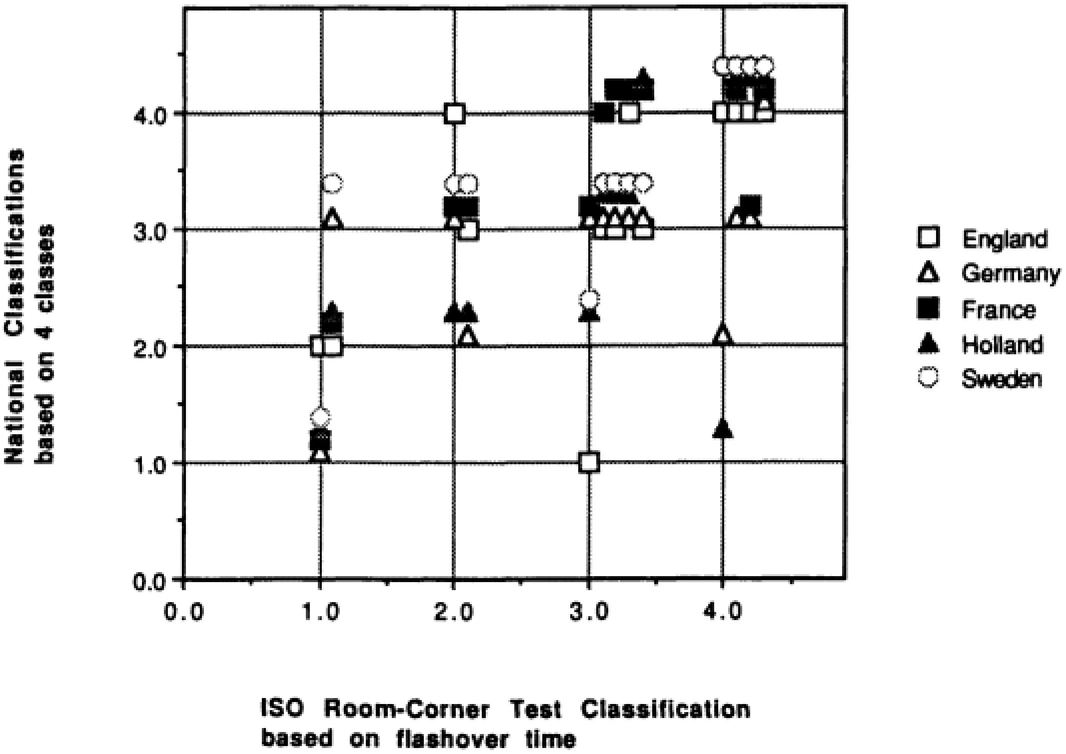

FIGURE 3 Comparison of the ISO Room-Corner Test with the National Test Classifications (Sundström and Göransson, 1988).

The results of these comparisons show that over one-third of the results are not consistent. This lack of agreement among standard national test methods, intending to measure the flammability of a material, is well known. By examining the materials and the results, it can be observed that low density materials fall into Class 4, wood products fall into Class 3, thin wall coverings fall into Class 2, and plasterboard is in Class 1. These are almost intuitively acceptable, but the materials and products that are not consistent raise many questions. The reasons probably vary and cannot easily be explained. But these reasons are significant to the lack of consistency and understanding between the test and the full-scale scenario.

Evaluation by Scientific Methods

Analyses of the ISO Room-Corner Test series (Sundström, 1986; Söderbom, 1991) by Karlsson (1992), Quintiere (1992), Wickström and Göransson (1992), and Quintiere et al. (1993) have produced theoretical methods to predict the full-scale results from material data from such tests as the Cone Calorimeter. These analyses provide a basis to quantitatively evaluate the hazard in terms of flashover and energy release rate. They provide an alternative classification method.

To illustrate this type of result, an empirical correlation, which was motivated by a more complete theoretical simulation (Quintiere, 1992; Quintiere et al., 1993), is presented. This gives an explicit formulation for flashover time in terms of components of the fire growth process significant for the ISO Room-Corner Test. The empirical correlation is presented as the dimensionless time to flashover: where $b = 0.01\,\dot{Q}'' - 1 - t_{ig}/t_b$. $\dot{Q}''$ is the energy release rate per unit area (kW/m^2) evaluated at an incident flux of 60 kW/m^2 indicative of the ignition heat flux in the ISO test, t_{ig} is the time to ignite at 30 kW/m^2 indicative of the heat flux for wall spread, and t_b is the burning time. These quantities can be computed from material property data deduced from the Cone Calorimeter.

$$t_{FO}/t_{ig} = f(b) \qquad (5)$$

The correlation results are shown for the ISO Room-Corner Test series (Sundström, 1986; Söderbom, 1991) in Figures 4a and 4b. Materials from a portion of that series make up Figure 3. Figure 4a shows the results in terms of the flashover time, and Figure 4b shows the results for the dimensionless time. Theory suggests flame spread accelerates for $b > 0$ and decays for $b < 0$. The empirical results indicate that for $b > \sim 0.40$, flashover time is solely dependent on ignition time. The reason for this simplified result is not obvious. A four-class ranking could be developed from these data as a function of *b,* but sensitivity of the results near $b = 0$ shows the exponential character of fire growth.

IMPORTANCE OF HEAT FLUX

From the previous correlation, it can be inferred that the selection of heat flux in the computations was crucial, especially to be consistent with the scenario. This is a central point of any testing strategy. The influence of heat flux on the fire-growth components for a material is also significant. Many test methods utilize a radiant heat source as the means to ignite and maintain flame spread and burning rate. The relationships between the test heat fluxes and the scenario need to be understood for the basis of a consistent hazard evaluation for materials.

Effect of Heat Flux on Fire-Growth Components

The time to ignite is inversely related to the imposed heat flux. Below a critical heat flux, ignition is not possible. Figure 5 shows an illustration of the piloted ignition of black polymethylmethacrylate (PMMA) under a specified irradiance (Rhodes, 1994). The data are fairly consistent with other literature sources and ideally should be apparatus independent. The solid lines show the application of a theory for different selected ignition temperatures.

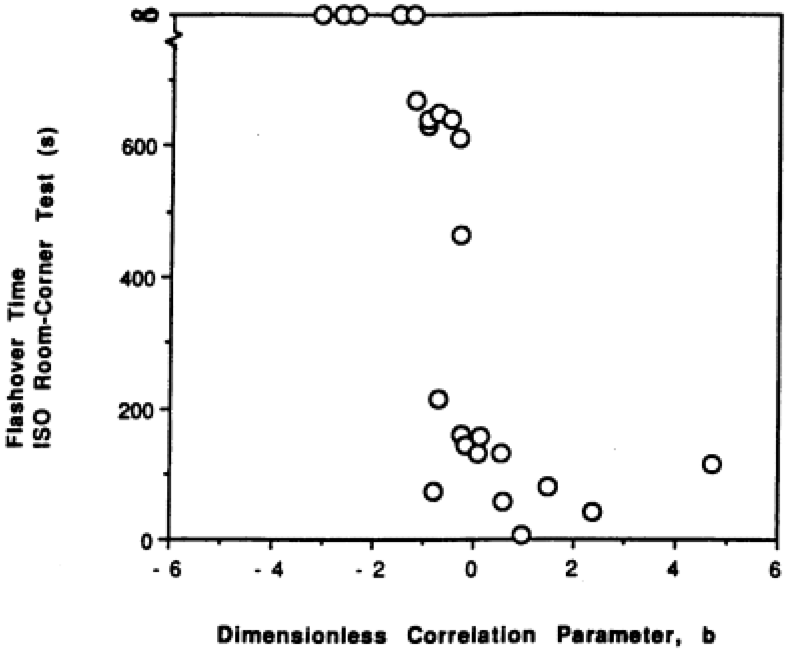

FIGURE 4a Correlation of flashover times in the ISO Room-Corner Test (Quintiere et al., 1993).

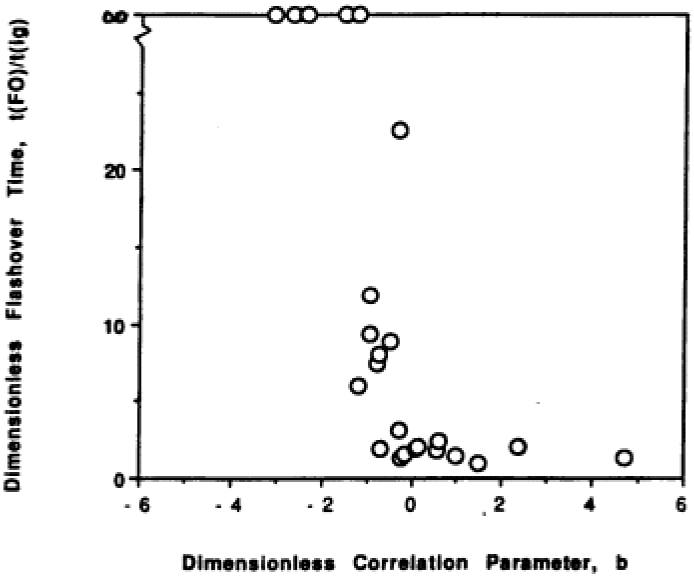

FIGURE 4b Dimensionless correlation for flashover in the ISO Room-Corner Test (Quintiere et al., 1993).

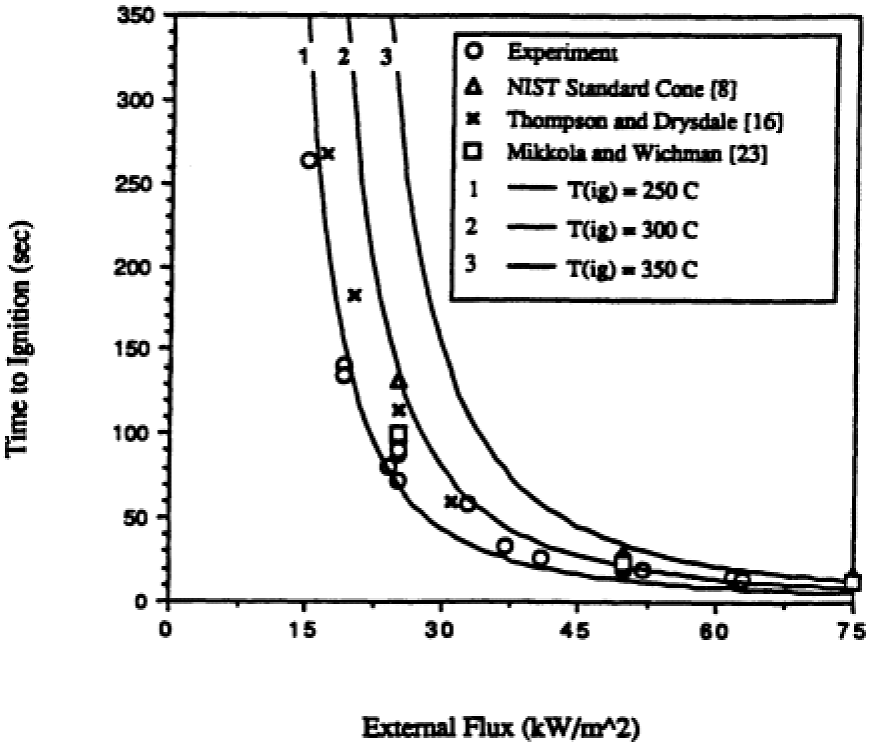

FIGURE 5 Effect of heat flux on the time to ignite (Rhodes, 1994).

Figure 6 shows how the steady mass-loss rate per unit area differs for various PMMA materials under external radiant heat fluxes for flaming and nonflaming cases (Rhodes, 1994). These results show an increase in burning rate due to flame heat flux, which in general depends on the burning configuration. They also show that different PMMA materials do not have the same vaporization response to heat flux (or that their heats of gasification differ).

Figure 7 shows results using various apparatuses and sample holder procedures to measure the peak energy release rate per unit area for polystyrene and thermoset foam materials (Cleary and Quintiere, 1991). These are small-scale tests (approximately 10 cm x 10 cm) that display serious sample holder effects for the polystyrene samples, as well as other issues of reproducibility. The results are not necessarily indicative of all materials but do dramatize the issues of reproducibility and small-scale sample edge effects.

The heat flux in the test method must be consistent with that in the fire scenario, or a methodology must exist to make the relationships. In some test methods, ignition is measured under an external radiant heat flux but with a contacting pilot flame of unknown heat flux. Such results can not be quantitatively useful and have no basis for comparison. Yet, a contacting pilot might be essential in some cases to ensure ignition under the conditions of that test method. Finally, it should be realized that, in general, the heat flux received by the material is composed of both the flame heat flux and the external radiant heat flux. This can be inferred from Figure 6 for the Cone Calorimeter, where it has been found that the flame heat flux for PMMA remains approximately constant at 37 kW/m² for a wide range of irradiance levels.

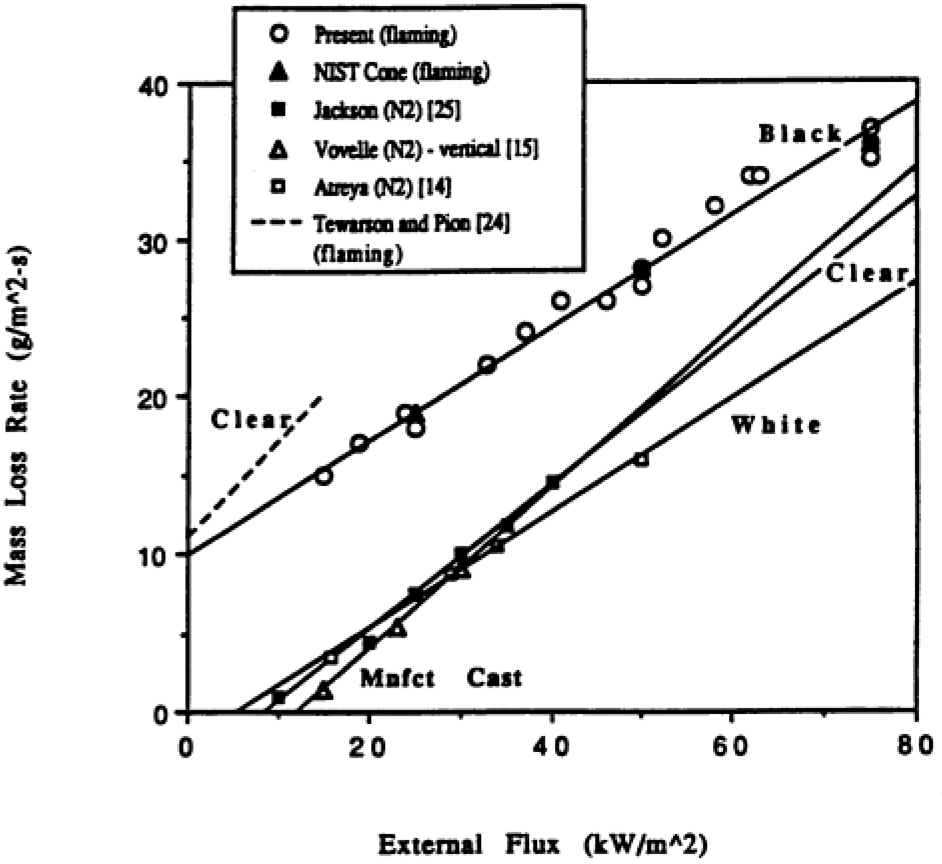

FIGURE 6 Effect of heat flux on burning rate (Rhodes, 1994).

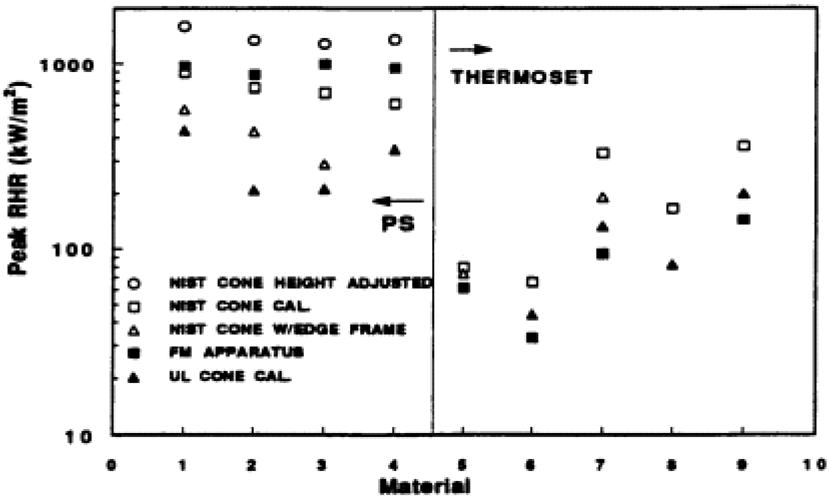

FIGURE 7 Lack of reproducibility in energy release rate for polystyrene and thermoset foams at 50 kW/m² irradiance (Clearly and Quintiere, 1991).

Heat Flux in Fire Scenarios

The ignition source in a fire scenario sets the initial heat flux and may even control the heat flux during early flame spread to flashover. The flame configuration after ignition will follow the configuration of the ignition source. Several recent reviews and studies (Kokkala et al., 1992; Back et al., 1994; Quintiere and Cleary, 1994) indicate the range of wall heat flux using square burners against walls and in corners. For square burners, the maximum flame heat flux is principally dependent on the energy release rate and roughly ranges from 40 to 120 kW/m² for 50 to 500 kW. The ISO Room-Corner Test burner appears to have a nominal maximum heat flux of 60 kW/m². Wall flames appear to have a maximum heat flux of 30 kW/m². Window flames appear to have heat fluxes as high as 200 kW/m² to facades. It should be clear that scenario heat fluxes vary significantly, and that hazard evaluations must match these heat flux conditions.

TESTING STRATEGIES

A valid testing strategy for hazard evaluation must have

- integrity with the scenario,
- integrity with the fire processes, and
- integrity with the hazard measure.

Products and materials must be tested at a sufficient size and configuration to be representative of the scenario, or analytical methods must exist to make predictions. The scenario must be examined to understand its parameters, and scenario testing must be done to establish these parameters and validation points. The strategy needs to be supported by scientific analysis as much as possible, and insupportable empirical approaches are not acceptable.

CONCLUSIONS

Fire hazard analyses for materials and products must be supported by the state of fire science. They need to be consistent with the scenario and representative of the material properties. Regulators and engineers must work together to ensure consistency between the hazard measures, the test method, and the scenario.

Measures of hazard relate to material properties and the burning rate. The burning rate or energy release rate is a reflection of "flammability," which includes ignition, flame spread, and the burning rate per unit area. These components are independent and depend on a distinct set of material properties and heat flux. It is the heat flux experienced by the material in a test and in a scenario that must be consistently considered. Current flammability tests are deficient since they do not provide a basis for analysis and do not necessarily correlate. Scientific approaches provide more generality but may be incomplete.

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Fire Properties of Materials

Archie Tewarson[*]

ABSTRACT

Fire properties of materials associated with the pyrolysis, ignition, combustion, fire propagation, and flame extinction processes are discussed. The relationships between the fire-hardening of materials and fire properties are enumerated. Fire-hardening is defined as a process where resistance to pyrolysis, ignition, combustion, and fire propagation is increased, and release rates of heat and fire products are decreased.

INTRODUCTION

Flammability is an interaction of pyrolysis, ignition, combustion, fire propagation, and flame extinction processes. The first four processes are brought about by the heat exposure of the material. The heat exposure must be of sufficient strength to satisfy the requirements of the pyrolysis process.

Pyrolysis is generally an endothermic process, characterized by the softening, melting, discoloration, cracking, decomposition, and vaporization and so forth of the material and release of products (i.e., smoke, toxic, and corrosive pyrolysis products). The boundary of the pyrolysis process is defined as the pyrolysis front.

Ignition is a process in which the pyrolysis products mix with air and form a combustible mixture, and the mixture ignites by itself (auto-ignition) or is ignited by a flame, a hot object, an electrical spark, or similar means (piloted ignition).

Combustion is a process in which the pyrolysis products react with oxygen from air, with a visible flame (flaming combustion). Heat and products (i.e., smoke and toxic and corrosive combustion products) are released in this process.

Fire propagation is a process in which the pyrolysis front, accompanied by the flaming or nonflaming combustion process, moves beyond the point of origin at a certain rate, defined as the fire-propagation rate. Heat and products (i.e., smoke and toxic and corrosive combustion products) are released at an increasing rate during the propagation process.

Flame extinction is a process in which the pyrolysis, ignition, combustion, and fire-propagation processes are interrupted by external agents such as water, Halon®, or alternatives. Heat and products are released at a decreasing rate until flame extinction. Pyrolysis products continue to be released past the flame extinction as long as the heat within the material continues to satisfy the requirements of the pyrolysis process.

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The release of heat and products (i.e., smoke and toxic and corrosive pyrolysis and combustion products) are hazardous to life and property. Hazard due to smoke and toxic and corrosive products is defined as nonthermal hazard (Tewarson, 1992). Hazard due to heat (i.e., high temperature and radiation) is defined as thermal hazard (Tewarson, 1992).

For protection of life and property from fires, materials need to be fire-hardened, and active and passive fire projections need to be provided. Fire-hardening is defined as a process in which resistance to pyrolysis, ignition, combustion, and fire propagation is increased, and release rates of heat and fire products are decreased. The fire-hardening requirements for the materials are considered in terms of the fire properties listed in Table 1. Fire-hardening can be achieved by several techniques of modifying the fire properties.

TABLE 1 Fire Properties of Materials to Assess Degree of Fire-Hardening

Fire Property	Description of the Fire Property
	Pyrolysis
Heat of gasification (ΔH_g)	Energy required to pyrolyze a unit mass of a material originally at ambient temperature
Surface re-radiation loss ($\dot{q}''_{rr}$)	Heat lost to the environment from the hot surface
Yield of a product	Amount of a product generated per unit mass of a material pyrolyzed
Product generation parameter	Amount of a product generated in pyrolysis per unit; amount of energy required to pyrolyze a unit mass of a material
	Ignition Process
Critical heat flux, ($\dot{q}''_{cr}$)	Minimum heat flux at or below which a flammable vapor-air mixture is not created
Thermal response parameter	Ease of in-depth penetration of the thermal wave and time delay to reach the ignition temperature
	Combustion Process
Flame heat flux ($\dot{q}''_f$)	Heat flux transferred from the flame back to the surface
Net heat of complete combustion (ΔH_T)	Amount of energy released in the complete combustion of a unit mass of a material pyrolyzed with water as gas
Chemical heat of combustion (ΔH_{ch})	Amount of energy actually released in a fire from the combustion of a unit mass of a material pyrolyzed
Convective heat of combustion (ΔH_{con})	Component of the chemical heat of combustion carried away from the flame by flowing combustion product-air mixture
Radiative heat of combustion (ΔH_{rad})	Component of the chemical heat of combustion transmitted away from the flame by radiation
Yield of a product	Amount of a product generated in the combustion per unit mass of a material pyrolyzed

Fire Property	Description of the Fire Property
Heat release parameter	Amount of energy generated in combustion per unit amount of energy required to pyrolyze a unit mass of a material
Product generation parameter	Amount of a product generated in combustion per unit; amount of energy required to pyrolyze a unit mass of a material
	Fire Propagation
Fire-propagation index	Extent and rate of fire propagation beyond the ignition zone
	Nonthermal Damage
Visibility through smoke (not defined)	Maximum distance over which an observer can see
Smoke damage (not defined)	Smoke damage due to discoloration, smell, or electrical malfunction
Toxic effects of products (not defined)	Toxic effects of products on humans
Corrosion damage by products— corrosion index	Rate of corrosion per unit mass concentration of a material pyrolyzed

PYROLYSIS

When a material is exposed to heat flux, pyrolysis products are generated. The rate of generation of the pyrolysis products is defined as the mass pyrolysis rate (Tewarson, 1988, 1994):

$$\dot{m}''_p = \frac{\dot{q}''_e - \dot{q}''_{rr}}{\Delta H_g} \qquad (1)$$

where $\dot{m}''_p$ is the mass pyrolysis rate in (kg/m^2·s), $\dot{q}''_e$ is the external heat flux (kW/m^2), $\dot{q}''_{rr}$ is the surface re-radiation loss (kW/m^2), and ΔH_g is the heat of gasification (MJ/kg).

The fire-hardening of materials requires that the values of surface re-radiation loss and heat of gasification be as high as possible.

Heat of Gasification

For a melting type of material, the heat of gasification is expressed as:

$$\Delta H_g = \int_{T_a}^{T_m} c_{p,s}\,dT + \Delta H_m + \int_{T_m}^{T_v} c_{p,l}\,dT + \Delta H_v \qquad (2)$$

where ΔH_m and ΔH_v are the heats of melting and vaporization at the respective melting and vaporization temperatures in MJ/kg; $c_{p,a}$, and $c_{p,1}$ are the specific heats of the solid and molten solids in MJ/kg, respectively; and T_a, T_m, and T_v are the ambient, melting, and vaporization temperatures in K, respectively. For materials that do not melt, but sublime, decompose, or char, Equation 2 is modified accordingly. Table 2 lists examples of the heat of gasification values taken from Tewarson 1988, 1994. The values are measured by differential scanning calorimetry (DSC) and by the mass pyrolysis technique using the Factory Mutual Research Corporation (FMRC) Flammability Apparatus shown in Figure 1.

Modifications in the pyrolysis behavior of the materials to increase the c_p, ΔH_m, and ΔH_v values and the melting and vaporization temperatures would increase the heat of gasification and reduce the mass pyrolysis rate (Equation 1) and other related fire properties.

Surface Re-Radiation Loss

Surface re-radiation loss is proportional to the fourth power of the pyrolysis temperature of the material. Stronger chemical bonds and pyrolysis mechanisms favoring retention of carbon in the solid phase (charring) would result in higher pyrolysis temperature and surface re-radiation. Mass pyrolysis rate decreases with increase in the surface re-radiation loss (Equation 1). Table 2 lists examples of the surface re-radiation loss taken from Tewarson 1988, 1994. The values are quantified by the mass pyrolysis technique in the FMRC Flammability Apparatus (Figure 1).

COMBUSTION

In the combustion process the pyrolysis products burn with air; a flame is established over the surface; and heat transferred from the flame back to the surface sustains the combustion process, with or without the external heat flux. For the combustion process, Equation 1 is expresse s (Tewarson, 1988, 1994): where $\dot{m}''_p$ is the mass pyrolysis rate in the combustion process (kg/m²·s), and $\dot{q}''_f$ is the flame heat flux transferred back to the surface (kW/m²).

$$\dot{m}''_p = \frac{\dot{q}''_e + \dot{q}''_f - \dot{q}''_{rr}}{\Delta H_g} \tag{3}$$

The fire-hardening of materials requires that the flame heat transferred back to the surface be reduced as much as possible.

Results from numerous small- and large-scale fires show that, as the surface area of the burning material increases, the flame radiative heat flux increases and reaches an asymptotic limit, whereas the flame convective heat flux decreases and becomes much smaller than the flame radiative heat flux at the asymptotic limit (Hottel, 1959). In small-scale experiments with fixed surface area, flame radiative heat flux increases and flame convective heat flux decreases with increase in the oxygen mass fraction (Y_o), as shown in Figure 2 (Tewarson et al., 1981).

TABLE 2 Surface Re-Radiation Loss and Heat of Gasification of Polymers

		Heat of Gasification (MJ/kg)	
Polymer	Surface Re-Radiation Loss (kW/m²)	Mass Pyrolysis Technique[a]	DSC
Polypropylene	15	2.0	2.0
Polyethylene (low density)	15	1.8	1.9
Polyethylene (high density)	15	2.3	2.2
Plasticized polyvinylchoride (PVC), LOI[b] = 0.20	10	2.5	-
Plasticized PVC, LOI = 0.30	-	2.1	-
Plasticized PVC, LOI = 0.35	-	2.4	-
Rigid PVC, LOI = 0.50	-	2.3	-
Polyoxymethylene	13	2.4	2.4
Polymethylmethacrylate	11	1.6	1.6
Polystyrene (granular)	13	1.7	1.8
Expanded polyurethane (flexible)	16-19	1.2-2.7	1.4

[a] From FMRC Flammability Apparatus (Figure 1). See Tewarson (1988, 1994) for other materials.

[b] LOI: Limiting Oxygen Index.

SOURCE: Data from Tewarson (1988, 1994).

For $Y_0 > 0.30$, the flame radiative heat flux reaches an asymptotic limit comparable to the limit for normal air burning in large-scale fires (Tewarson et al., 1981; Tewarson, 1988, 1994). Thus, large-scale flame radiative heat flux conditions can be simulated in small-scale experiments.

The technique to simulate large-scale flame radiative heat flux conditions in small-scale flammability experiments by the oxygen mass fraction variations is defined as the Flame Radiation Scaling Technique (Tewarson, 1988, 1994).

Table 3 compares the results from the flame radiation scaling technique used in the small-scale experiments in the FMRC Flammability Apparatus and results from large-scale fires. The data show that the asymptotic flame heat flux values from the FMRC Flammability Apparatus are in good agreement with the values derived from the mass pyrolysis rate in large-scale fires. The asymptotic flame heat flux values vary from 22 kW/m² to 77 kW/m², dependent primarily on the pyrolysis mode rather than on the chemical structures. For example, for liquids, which vaporize primarily as monomers, the asymptotic flame heat flux values are in the range of 22 kW/m² to 44 kW/m², irrespective of their chemical structures. For polymers, which vaporize as high molecular weight oligomers, the asymptotic flame heat flux values increase substantially to the range of 49 kW/m² to 71 kW/m², irrespective of their chemical structures. The independence of the asymptotic flame heat value from the chemical structure is consistent with the dependence of the flame radiation on optical thickness, soot concentration, and flame temperature.

Modifications in the pyrolysis behavior to enhance release of higher monomer fraction relative to oligomer fraction and reduction in the carbon atom fraction relative to other atoms in the pyrolysis products (enhanced surface charring) would reduce the flame heat flux transferred back to the surface and the mass pyrolysis rate (Equation 3).

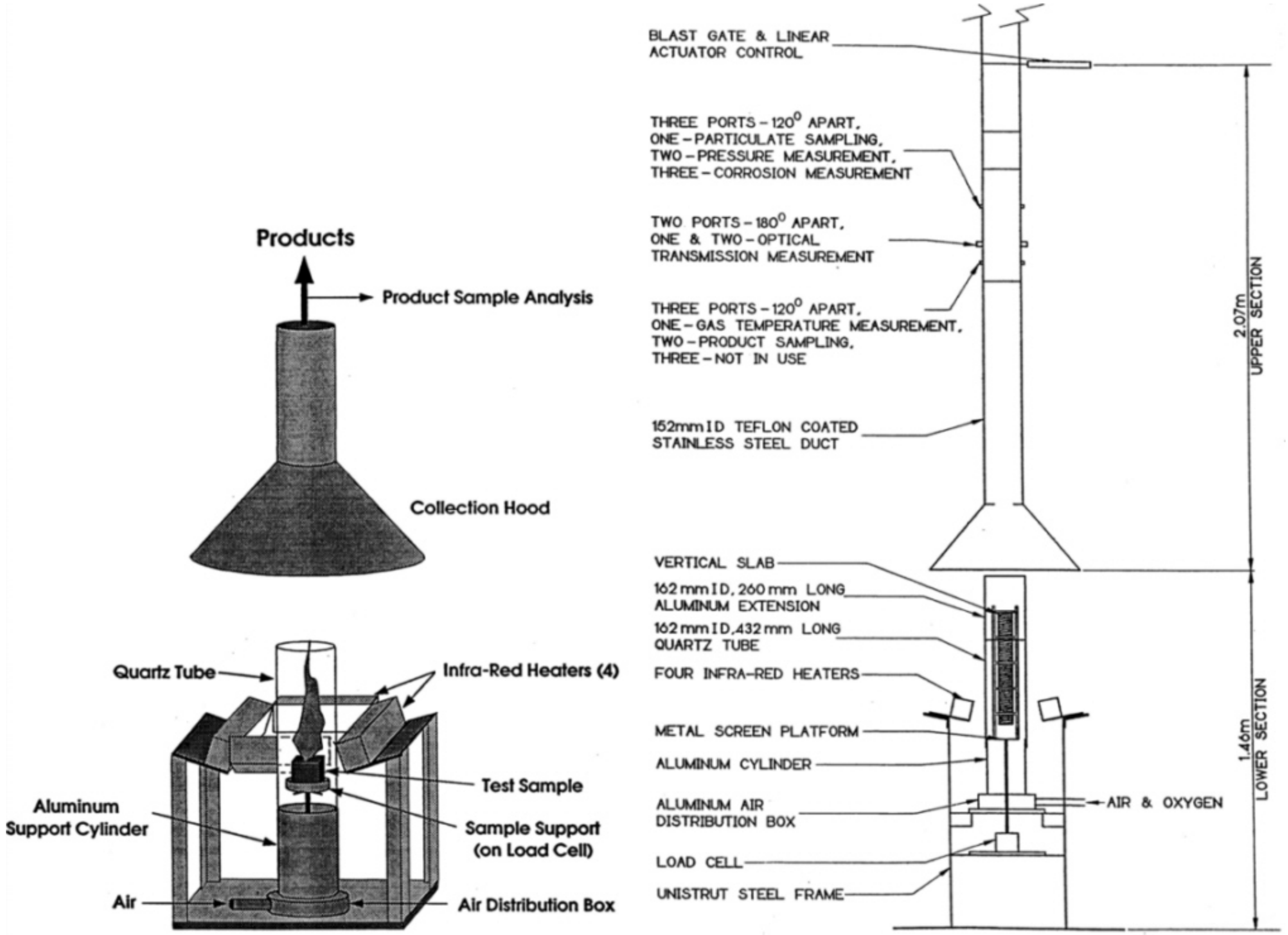

FIGURE 1 The Factory Mutual Research Corporation's (FMRC) Flammability Apparatus (50 kW-scale) showing details of sample configuration for ignition, pyrolysis, and combustion experiments.

The mass pyrolysis rate is directly proportional to the heat release rate and the generation rates of products. Decrease in the mass pyrolysis rate, thus, would reduce the thermal and nonthermal hazards.

IGNITION

Ignition is a process in which the pyrolysis products are generated at a certain rate, mix with air, and form a combustible mixture that ignites by itself (auto-ignition) or is ignited by a flame, a hot object, or similar means (piloted ignition). The rate of generation of the pyrolysis products leading to ignition is defined as the critical mass pyrolysis rate. Minimum heat flux at or below which the critical mass pyrolysis rate is not achieved and there is no ignition is defined as the critical heat flux (CHF). The CHF value is very close to the surface re-radiation loss.

Relationships have been developed between the time to ignition and external heat flux (Tewarson, 1988). These relationships are as follows: (1) for thermally thick materials, the surface is at the ignition temperature and the back is close to the ambient temperature at the ignition condition; and (2) for thermally thin materials, the surface is at the ignition temperature and the back is close to the ignition temperature at the ignition condition.

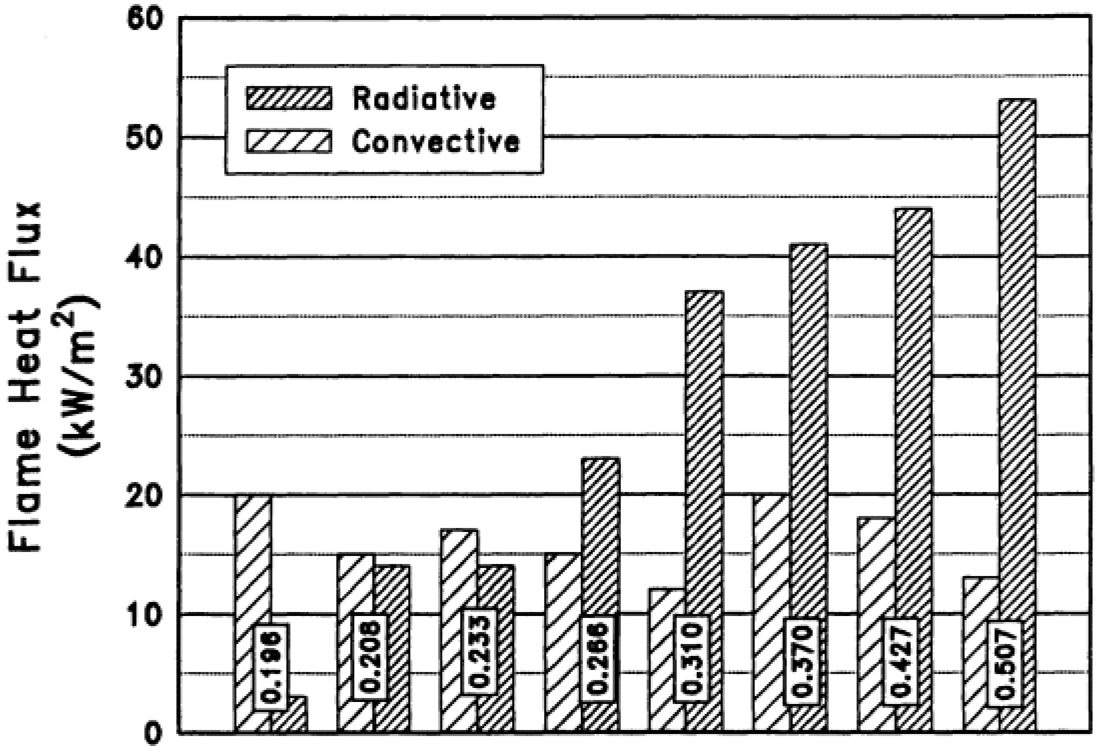

FIGURE 2 Flame radiative and convective heat fluxes at various oxygen mass fractions for the steady-state combustion of 100 x 100 x 25-mm-thick slab of polypropylene. Data are from the FMRC Flammability Apparatus. Numbers are the oxygen mass fractions.

TABLE 3 Asymptotic Mass Pyrolysis Rate and Flame Heat Flux in Combustion

	Mass Pyrolysis Rate $(kg/m^2 \cdot s) \times 10^3$		Flame Heat Flux (kW/m^2)	
Polymers/Liquids[a]	Flame Radiation Scaling Technique[a]	Large-Scale	Flame Radiation Scaling Technique[a]	Large-Scale
	Aliphatic Carbon-Hydrogen Atoms			
Polyethylene	26	-	61	
Polypropylene	24	-	67	
Heavy fuel oil (2.6-23 m)[b]	-	36	-	29
Kerosene (30-80 m)	-	65	-	29
Crude oil (6.5-31 m)	-	56	-	44
n-Dodecane (0.94 m)	-	36	-	30
Gasoline (1.5-223 m)	-	62	-	30
JP-4 (1.0-5.3 m)	-	67	-	40
JP-5 (10.60-17 m)	-	55	-	39
n-Heptane (1.2-10 m)	~66	75	32	37
n-Hexane (0.75-10 m)	-	77	-	37
Transformer fluids (2.37 m)	27-30	25-29	23-25	22-25
	Aromatic Carbon-Hydrogen-Oxygen Atoms			
Polystyrene (0.93 m)	36	34	75	71
Xylene (1.22 m)	-	67	-	37
Benzene (0.75-6.0 m)	-	81	-	44
	Aliphatic Carbon-Hydrogen-Oxygen Atoms			
Polyoxymethylene	16	-	50	
Polymethylmethacrylate (2.37 m)	28	30	57	60
Methanol (1.2-2.4 m)	20	25	22	27
Acetone (1.52 m)	-	38	-	24
	Aliphatic Carbon-Hydrogen-Oxygen-Nitrogen Atoms			
Expanded polyurethanes (flexible)	21-27	-	64-76	
Expanded polyurethanes (rigid)	22-25	-	49-53	
	Aliphatic Carbon-Hydrogen-Halogen Atoms			
Polyvinylchloride (PVC)	16	-	50	
Ethylenetetrafluoroethylene (ETFE) (Tefzel)	14	-	50	
Fluorinated ethylene-propylene (FEP) (Teflon)	7		52	

[a] Flame Radiation Scaling Technique: Pool diameter fixed at 0.10 m, $Y_o \geq 0.30$.

[b] Numbers in parentheses are the pool diameters in meters.

SOURCE: Data from Tewarson (1988, 1994).

Ignition of Thermally Thick Materials

$$\sqrt{\frac{1}{t_{ig}}} = \sqrt{\frac{\pi}{4}}\,\frac{\dot{q}''_{e} - \dot{q}''_{cr}}{\Delta T_{ig}\sqrt{k\rho c_{p}}} \qquad (4)$$

where t^{ig} is the time to ignition (s), , $\dot{q}_{cr}$ is the critical heat flux (kW/m²), ΔT_{ig} is the ignition temperature of the material above the ambient temperature (K), k is the thermal conductivity of the material (kW/m·K), *p* is the density of the material (kg/m^3), and c_p is the specific heat of the material (MJ/kg K). $\Delta T_{ig}\sqrt{\ } k\rho c_p$ is defined as the thermal response parameter (TRP) for the thermally thick material (kW·s$^{1/2}$/m²).

For thermally thick materials, the square root of time to ignition is directly proportional to TRP and inversely proportional to the external heat flux. Figure 3 shows a typical example of the data for a thermally thick polymethylmethacrylate (PMMA) slab at various velocities (v_g) of the co-flowing air.

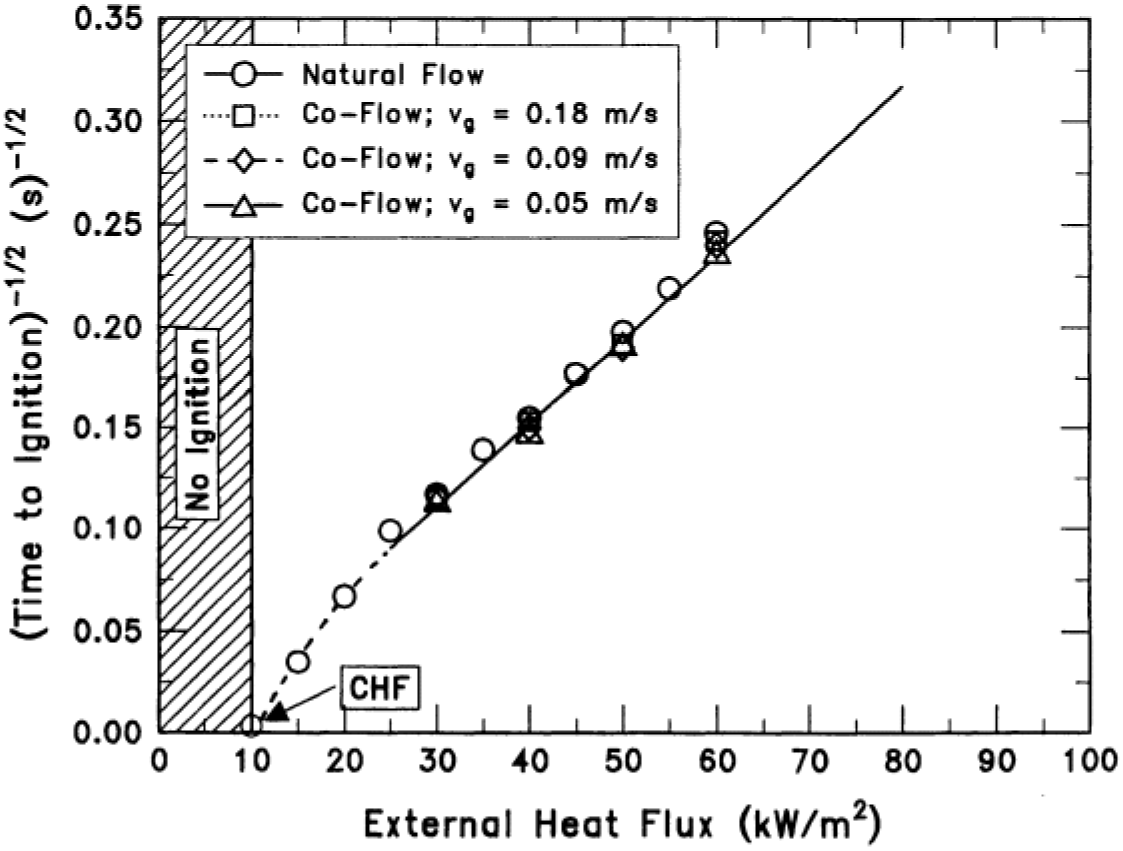

FIGURE 3 Ignition data for 100 x 100 x 25-mm thick polymethylmethacrylate (PMMA) slab with blackened surface. Data measured in the FMRC Flammability Apparatus.

Ignition of Thermally Thin Materials

$$\frac{1}{t_{ig}} = \frac{\pi}{4} \frac{\dot{q}''_e - \dot{q}''_{cr}}{\rho c_p \delta \Delta T_{ig}} \qquad (5)$$

where δ is the actual thickness of the material (m). The TRP for the thermally thin material (kJ/m²) is defined as $\rho c_p \delta \Delta T_{ig}$

For thermally thin materials, the time to ignition is directly proportional to TRP and inversely proportional to the external heat flux.

The fire-hardening of materials requires that the values of the CHF and the TRP be as high as possible. The CHF and TRP values have been reported for numerous natural and synthetic materials (Tewarson, 1988, 1994).

Thermal Response Parameter (TRP)

The TRP values depend on the physical and chemical characteristics of the materials. An example is shown in Figure 4, where the TRP value is plotted against the resin fractions of the

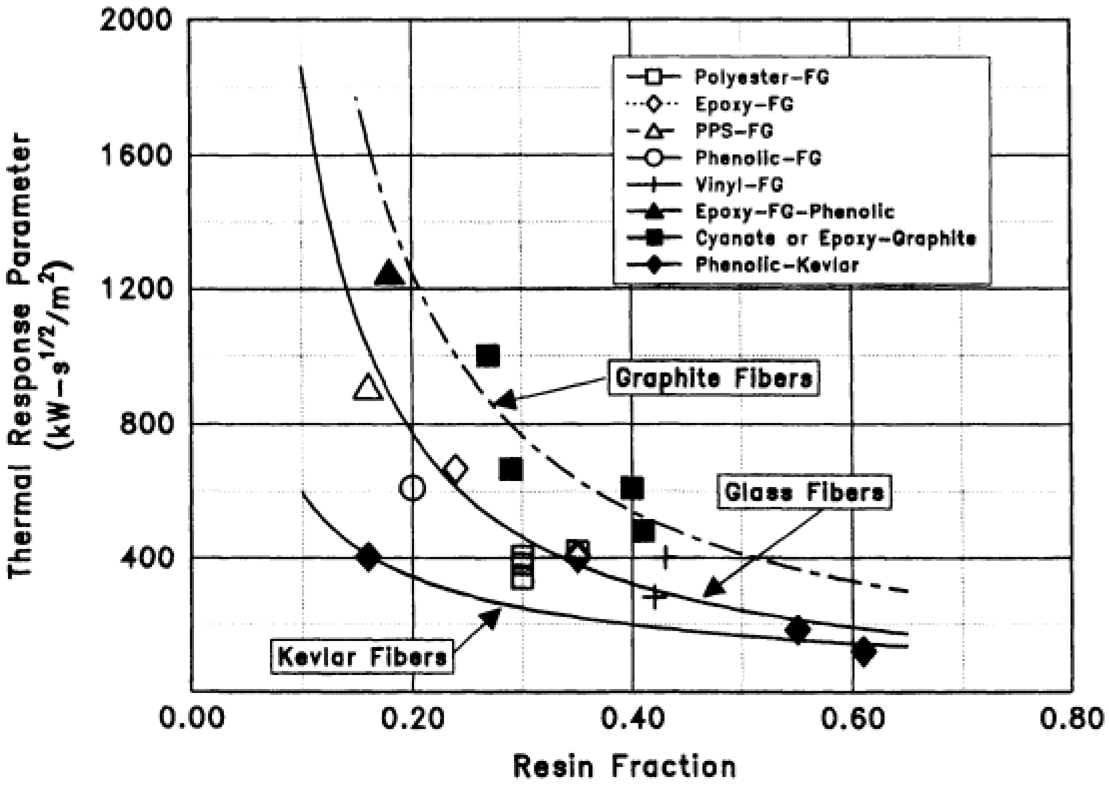

FIGURE 4 Thermal response parameter (TRP) versus the resin fraction for the composite systems. Data are from the FMRC Flammability Apparatus.

composite systems. The TRP values increase with decrease in the resin fraction and increase in the fiber fraction. For the same resin fraction, the TRP value is highest for the graphite fiber systems, intermediate for the glass fiber systems and lowest for the Kevlar® fiber system, following the trends in the thermal conductivities of the fibers, that is, graphite > glass > Kevlar®. For higher thermal conductivity fibers, a larger fraction of the heat applied to the surface is transferred to the interior, and time required to reach the ignition temperature is longer, resulting in the higher TRP value.

The residual flexural strength retained (RFSR) is one of the parameters used to assess the structural performance of the composite systems (Sorathia et al., 1993). The dependency of RFSR on the properties of the composite systems is very similar to the dependency of TRP. A relationship between the RFSR and the TRP has thus been postulated (Tewarson and Haskell, 1994).

Variations in the chemical bonds within similar generic resins and additives also play a major role in the ignition behavior of the composite systems by affecting the TRP values, as indicated by the data in Table 4 for fiberglass-reinforced polyester and epoxy composite systems.

FIRE PROPAGATION

Fire propagation is a process in which the pyrolysis front moves beyond the ignition zone, accompanied by the sustained combustion process. The rate of the movement of the pyrolysis front is defined as the fire-propagation rate. For a sustained fire-propagation process, flame or external heat sources need to transfer heat flux ahead of the pyrolysis front to satisfy the CHF and TRP values.

The upward fire-propagation rate in the direction of air flow for thermally thick materials is expressed as (Sibulkin and Kim, 1977):

$$u^{1/2} = \frac{\delta_f^{1/2}\, \dot{q}''_f}{\Delta T_{ig}\sqrt{(k\rho c_p)}} \qquad (6)$$

where u is the fire-propagation rate in m/s; δ_f is an effective flame heat transfer distance (m), assumed to be constant; $\dot{q}''_f$ is the flame heat flux transferred ahead of the pyrolysis front (kW/m²); and $\Delta T_{ig}\sqrt{k\rho c_p}$ is the TRP for the thermally thick materials in $\text{kW·s}^{1/2}/\text{m}^2$ (Equation 4).

The flame heat flux transferred ahead of the pyrolysis front is a function of the rate of heat actually released in the fire-propagation process, defined as the *chemical heat release rate.* Figure 5 shows an example of the chemical heat release rate for the downward fire propagation for a 300-mm long, 100-mm wide, and 25-mm-thick vertical slab of PMMA in an oxygen mass fraction of 0.446 (Tewarson and Ogden, 1992). The slope of the curve is the fire-propagation rate. The figure also shows the combustion of the entire slab in normal air and in reduced oxygen mass fractions. The flame extinction occurs at an oxygen mass fraction of 0.178.

TABLE 4 CHF and TRP for Thermally Thick Composites with Fiberglass Reinforcement

Fiberglass (weight %)	CHF (kW/m²)	TRP (kW·$s^{1/2}$/m^2)
	Polyester	
0		296
30	-	256
70 (1)	10	275
70 (2)	10	382
70 (3)	15	406
70 (4)	10	338
77	-	426
	Epoxy	
0	-	257
65 (1)	10	420
65 (2)	10	410
65 (3)	10	400
76	15	667

SOURCE: Data from Tewarson (1988, 1994).

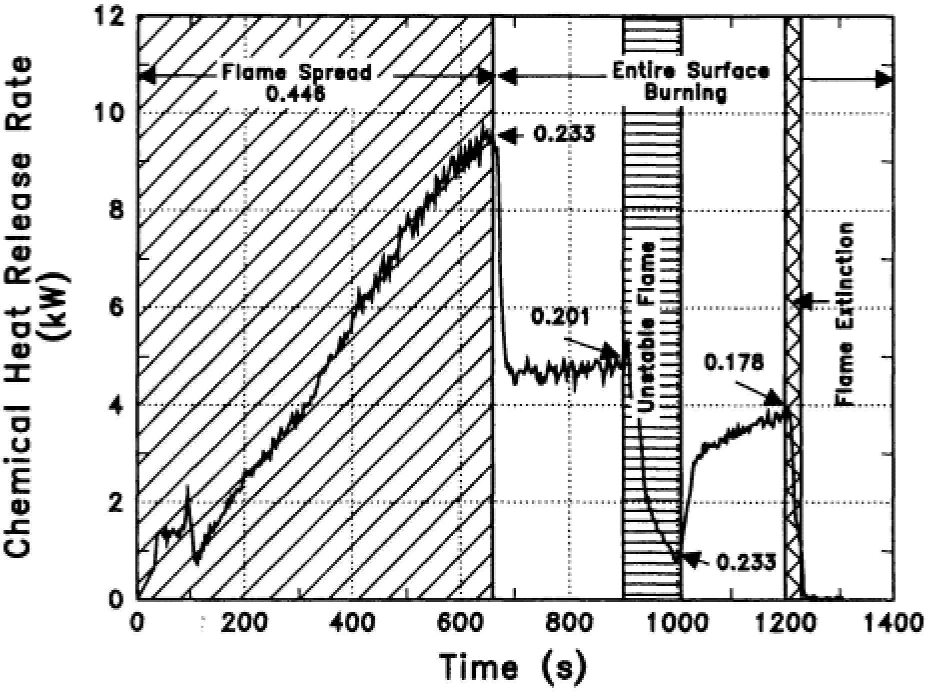

FIGURE 5 Chemical heat release rate versus time for the downward fire propagation, steady combustion, and flame extinction for 300-mm long, 100-mm wide, and 25-mm-thick PMMA vertical slab under opposed air flow condition in the FMRC Flammability Apparatus. Air flow velocity = 0.09 m/s. Numbers are oxygen mass fractions.

The chemical heat released in the fire-propagation process has a convective and a radiative component. In larger-scale fires the flame heat flux transferred ahead of the pyrolysis front is mainly a function of the radiative component of the chemical heat release rate or the radiative heat release rate.

Numerous correlations have been developed for the relationship between the flame heat flux transferred ahead of the pyrolysis front and the radiative heat-release rate, one of which is (Tewarson and Khan, 1988): where $\dot{Q}'_{rad}$ is the radiative heat release rate per unit width or circumference of a slab or a cylinder of a material respectively (kW/m). From the definition of the radiative heat release rate (Tewarson, 1988, 1994): where χ_{rad} is the radiative component of the combustion efficiency, χ_{ch}, $\dot{Q}'_T$ is the heat release rate for complete combustion per unit width or circumference of the slab or cylinder of the material, respectively (kW/m); $\dot{Q}'_{ch}$ is the chemical heat release rate per unit width or circumference of the slab or cylinder of the material, respectively (kW/m); ΔH_{ch} is the chemical heat of combustion (MJ/kg); and ΔH_{rad} is the radiative heat of combustion (MJ/kg). The average value of $\Delta H_{rad} = 0.42 \pm 0.13$ (Tewarson, 1988, 1994) and, from equations 7 and 8: and, from equations 6 and 9:

$$\dot{q}''_f \propto (\dot{Q}'_{rad})^{1/3} \tag{7}$$

$$\dot{Q}'_{rad} = \chi_{rad}\dot{Q}'_T = (\chi_{rad}/\chi_{ch})\dot{Q}'_{ch} = (\Delta H_{rad}/\Delta H_{ch})\dot{Q}'_{ch} \tag{8}$$

$$\dot{q}''_f \propto (0.42Q_{ch}')^{1/3} \tag{9}$$

$$u^{1/2} \propto \frac{(0.42\dot{Q}'_{ch})^{1/3}}{\Delta T_{ig}\sqrt{k\rho c_p}} \tag{10}$$

The righthand side of Equation 10, with a proportionality constant assumed to be 1,000, $\dot{Q}'_{ch}$ in kW/m and $\Delta T_{ig}\sqrt{k\rho c_p}$ in kW·s$^{1/2}$/m^2 is defined as *the fire-propagation index* (FPI) (Tewarson, 1988, 1994):

$$FPI = \frac{1{,}000(0.42\dot{Q}'_{ch})^{1/3}}{TRP} \tag{11}$$

Fire-Propagation Index

The following FPI values, based on the data from small- and large-scale fires, have been found to characterize the general fire-propagation behavior of materials under high flame radiation conditions:

- FPI ≤ 7: No fire propagation beyond the ignition zone. Polymers are identified as nonpropagating group N-1 polymers. Flame is at critical extinction condition.
- 7< FPI < 10: Decelerating fire propagation beyond the ignition zone. Polymers are identified as group D-1 polymers. Fire propagates beyond the ignition zone although in a decelerating fashion. Fire propagation beyond the ignition zone is limited.
- 10 ≤ FPI < 20: Fire propagates slowly beyond the ignition zone. Polymers are identified as propagating group P-2 polymers.
- FPI ≥ 20: Fire propagates rapidly beyond the ignition zone. Polymers are identified as propagating group P-3 polymers.

The fire-hardening of materials requires that the FPI values of the materials be less than or equal to 7. Examples of some typical FPI values are listed in Table 5.

TABLE 5 Fire-Propagation Index of Materials

Polymers	Thickness (mm)	FPI	Group	Fire Propagation[a]
	Polymers			
Polymethylmethacrylate	25	30	P-3	P
Fire-retarded polypropylene	25	>>10	P-3	P
PVC/PVF cable	5 (diameter)	7	*N-1*	N
FEP/FEP cable	10 (diameter)	5	N-1	N
	Composite Systems			
Polyester1-70% FG[b]	4.8	13	P-2	P
	4.8	10	P-2	P
Polyester2-70% FG	19	8	D-1	D
	45	7	N-1	N
Epoxy1-65% FG	4.4	9	D-1	D
Epoxy2-65% FG	4.8	11	P-2	P
Epoxy3-65 % FG	4.4	10	P-2	P
Phenolic-80% Kevlar®	3.2	3	*N-1*	N
Phenolic-84% Kevlar®	4.8	8	D-1	D

[a] P: propagating; D: decelerating propagation; N: nonpropagating.

[b] FG: fiberglass.

SOURCE: Data from Tewarson (1988, 1994).

The FPI is inversely proportional to the first power of the TRP value and directly proportional to the one-third power of the chemical heat release rate. Thus, the TRP value has a much stronger effect on the FPI value than the chemical heat release rate. An increase in the TRP value and a decrease in the chemical heat release rate by the various techniques discussed in the previous sections would lead to FPI values that are £ 7.

GENERATION OF HEAT AND FIRE PRODUCTS

As a material is exposed to heat in the ignition zone, the first step is the generation of the pyrolysis products. The second step is the mixing of the pyrolysis products and air and the ignition of the mixture. The third step is the establishment of sustained combustion as a result of the burning of the pyrolysis products with air. The fourth step is the movement of the pyrolysis front beyond the ignition zone as a result of the heat transfer from the flame or external heat source beyond the ignition zone. Heat and fire products (i.e., smoke, toxic, and corrosive) are generated in each of the above steps.

Heat Release Rate

The chemical heat release rate is directly proportional to the mass pyrolysis rate in the combustion process, defined in Equation 3: where Q''_{ch} is the chemical heat release rate (kW/m²) and ΔH_{ch} is the proportionality constant defined as the chemical heat of combustion (MJ/kg). ΔH_{ch} is always less than the net heat of complete combustion, ΔH_T because, as in fires, the combustion process always remains incomplete. The ratio $\Delta H_{ch} / \Delta H_T$ is defined as the combustion efficiency, χ_{ch} The convective and radiative components of the chemical heat release rate and chemical heat of combustion are defined as the convective and radiative heat release rates, Q''_{con} and Q''_{rad} and convective and radiative heat of combustion, ΔH_{con} and ΔH_{rad}, respectively. The convective and radiative components of the combustion efficiency are expressed as, χ_{con} and χ_{rad}, respectively. Data for the heats of combustion for a variety of materials have been reported (Tewarson, 1988, 1994).

$$\dot{Q}''_{ch} = \Delta H_{ch} m''_p \qquad (12)$$

The chemical heat of combustion decreases, but combustion efficiency increases with the introduction of the oxygen atom into the carbon and hydrogen atom containing chemical structures of the materials. The combustion efficiency decreases, but its radiative component increases with the increase in the chemical bond unsaturation and aromaticity and with introduction of the halogen, sulfur, and nitrogen atoms in the structures of the materials.

The fire-hardening of materials requires that the heats of combustion be reduced to values as low as possible. Techniques to retain large fractions of the carbon atoms in the solid phase (charring), introduction of the oxygen atoms in the chemical structures, and enhancement of the chemical bond saturation may be helpful, similar to the techniques to increase the heat of gasification discussed previously.

Heat Release Parameter

From equations 3 and 12:

$$\dot{Q}''_{ch} = \left[\frac{\Delta H_{ch}}{\Delta H_g}\right](\dot{q}''_e + \dot{q}''_f - \dot{q}''_{rr}) \qquad (13)$$

The ratio of the chemical heat of combustion to heat of gasification, ΔH_{ch} / ΔH_g is defined as the *heat release parameter* (HRP) in MJ/MJ. The HRP defines the amount of energy generated in combustion per unit amount of energy required to pyrolyze a unit mass of the material. HRP has a convective and a radiative component. The HRP value is independent of the fire size but depends on the fire ventilation.

The fire-hardening of materials requires that the HRP be reduced to values as low as possible. HRP values for numerous materials have been published (Tewarson, 1988, 1994). Selective data from this tabulation are listed in Table 6. *The data suggest that the nonpropagating fire condition is satisfied when* HRP ≤ 2.

TABLE 6 Fire-Propagation Index and Heat Release Parameter for Selected Materials

Polymers	Thickness (mm)	FPI	Group	HRP
	Polymers			
Polymethylmethacrylate	25	30	P-3	15
Fire-retarded polypropylene	25	>> 10	P-3	19
PVC/PVF cable	5 (diameter)	7	N-1	1
FEP/FEP cable	10 (diameter)	5	N-1	2
	Composite Systems			
Polyester1-70% FG[a]	4.8	13	P-2	5
Polyester2-70% FG	4.8	10	P-2	-
	19	8	D-1	-
	45	7	N-1	2
Epoxyl-65% FG	4.4	9	D-1	6
Epoxy2-65% FG	4.8	11	P-2	5
Epoxy3-65% FG	4.4	10	P-2	6
Phenolic-80% FG	3.2	3	N-1	1
Phenolic-84% Kevlar®	4.8	8	D-1	4

[a] FG: fiberglass.

SOURCE: Data from Tewarson (1988, 1994).

The Effect of Ventilation on the HRP

The effect of ventilation on the HRP values of the nonhalogenated materials is expressed as (Tewarson et al., 1993): where $(HRP)_v$ is the ventilation-controlled combustion value, and $(HRP)_\infty$ is the well-ventilated combustion value; φ is the equivalence ratio:

$$(HRP)_v = (HRP)_\infty \left[\frac{1-0.97}{\exp(\phi/2.2)^{-1.2}} \right] \qquad (14)$$

$$\Phi = \frac{S\dot{m}''_p A}{\dot{m}_{air}} \qquad (15)$$

where S is the stoichiometric mass air-to-fuel ratio (kg/kg), A is the exposed surface area of the burning material (m^2), and $\dot{m}_{air}$ is the mass flow rate of air (kg/s). Figure 6 shows the ratio of $(HRP)_v$ to $(HRP)_\infty$ as a function of the equivalence ratio. For □ ≥ 1.0, $(HRP)_v$ / $(HRP)_\infty$£ 1.0, an indication of ventilation-controlled combustion. For □≥4, the HRP value becomes less than about 40 percent of the HRP value for well-ventilated combustion, and flame is extinguished.

Equation 14 provides a relationship to determine the HRP values for various fire ventilation conditions. By knowing or predicting the net heat flux for a fire scenario, the chemical heat release rate can be calculated from Equation 13.

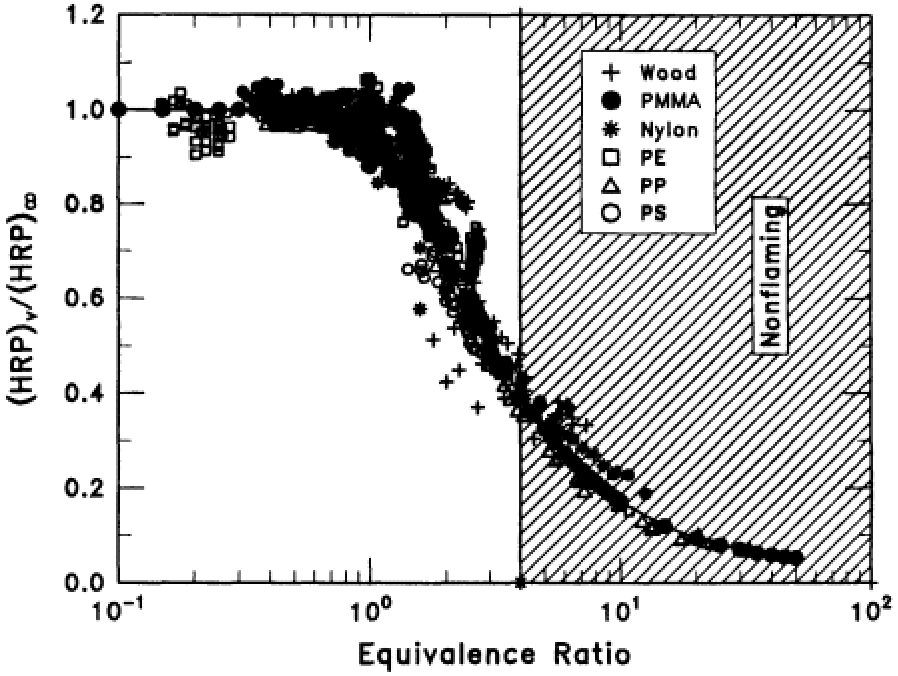

FIGURE 6 Ratio of the heat release parameter for the ventilation-controlled to well-ventilated combustion of materials versus the equivalence ratio.

Mass Generation Rate of a Product

The mass generation rate of a product in pyrolysis or combustion is directly proportional to the mass pyrolysis rate: where $\dot{G}''_j$ is the mass generation rate of product j (kg/m²·s), and y_j the proportionality constant, is defined as the yield of the product (kg/kg). Yields of CO, CO_2, hydrocarbons, and smoke for a variety of materials have been reported (Tewarson, 1988, 1994). The yields of products of incomplete combustion, that is, CO, hydrocarbons, and smoke, increase with increase in the chain length and chemical bond unsaturation and aromaticity and with introduction of the halogen, sulfur, and nitrogen atoms in the structures of the materials.

$$\dot{G}''_j = y_j \dot{m}''_p \qquad (16)$$

In fires the yield of a product is significantly less than its *stoichiometric yield, defined as the maximum possible conversion of the material to the product:* where Ψj is the stoichiometric yield of product j, M_j is the molecular weight of product (kg/mole), and M_f is the molecular weight of the pyrolyzed material assumed to be a monomer (kg/mole). The stoichiometric yields of products depend on the relative numbers of hydrogen, oxygen, nitrogen, sulfur, halogen, and other atoms relative to the carbon atom. The stoichiometric yields of the products provide an insight into the nature of the products and the maximum possible mass generation rates of products expected in pyrolysis and combustion processes in fires. The ratio $y_j/\Psi j$ is defined as the generation efficiency of the product j, η_j

$$\Psi_j = \frac{\nu_j M_j}{M_p} \qquad (17)$$

The fire-hardening of materials requires that the yields of products of complete and incomplete combustion and pyrolysis be reduced to values as low as possible. Techniques to reduce the heats of combustion and gasification, discussed previously, would also help to reduce the yields of the products.

Product Generation Parameter

For the pyrolysis process, from equations 1 and 15

$$\dot{G}''_j = \left[\frac{y_j}{\Delta H_g}\right](\dot{q}''_e - \dot{q}''_{rr}) \qquad (18)$$

For the combustion process, from equations 3 and 15

$$\dot{G}''_j = \left[\frac{y_j}{\Delta H_G}\right] (\dot{q}''_e + \dot{q}''_f - \dot{q}''_{rr}) \qquad (19)$$

The ratio of the yield of a product to heat of gasification, $y_j / \Delta H_g$ is defined as the *product generation parameter* (PGP) in kg/MJ. The PGP defines the amount of a product generated per unit amount of energy required to pyrolyze the material. PGP is independent of the fire size but depends on the fire ventilation.

The fire-hardening of materials requires that the PGP values for products of complete and incomplete combustion and pyrolysis be reduced to values as low as possible. Techniques to reduce the HRP values, discussed previously, would also help to reduce the PGP values.

The CO and smoke PGP values for selected materials are listed in Table 7, along with the FPI values and the group classification. *Within each fire-propagation group, fire-hardening requires that the CO and smoke PGP be reduced to as low values as possible through various techniques.*

TABLE 7 Fire-Propagation Index and Product Generation Parameter for Selected Materials

Polymers	Thickness (mm)	FPI	Group	PGP, CO	PGP, Smoke
	Synthetic Polymers				
Polymethylmethacrylate	25	30	P-3	0.0062	0.014
Fire-retarded polypropylene	25	>> 10	P-3	0.012	0.029
PVC/PVF	5 (diameter)	7	N-1	-	-
FEP/FEP cable	10 (diameter)	5	N-1	0.085	0.002
	Composite Systems				
Polyester l-70% FG[a]	4.8	13	P-2	0.017	0.021
	4.8	13	P-2	0.056	0.037
Polyester 2-70% FG	19	8	D-1	-	-
	45	7	N-1	-	-
Epoxy 1-65% FG	4.4	9	D-1	0.088	0.068
Epoxy 2-65% FG	4.8	11	P-2	0.053	0.088
Epoxy 3-65% FG	4.4	10	P-2	0.072	0.052
Phenolic-80% FG	3.2	3	N-1	0.007	0.002
Phenolic-84% Kevlar®	4.8	8	D-1	0.002	0.003

[a] FG: fiberglass.

SOURCE: Data from Tewarson (1988, 1994).

The Effect of Ventilation on the PGP

The effect of ventilation on the HRP values of the nonhalogenated materials is expressed as (Tewarson et al., 1993): where $(PGP)_{j,v}$ is the product *j* PGP value for ventilation-controlled combustion (kg/MJ), $(PGP)_{j,\infty}$ is the product *j* PGP value for well-ventilated combustion (kg/MJ), and α, ß, and ξ are the ventilation correlation coefficients. The values of α, ß and ξ for CO, CO_2, O_2, hydrocarbons, and smoke for various materials have been reported (Tewarson, 1988, 1994). The values of α and ξ are strongly dependent; whereas, the value of ß is weakly dependent on the chemical structures of the nonhalogenated materials.

$$(PGP)_{j,v} = (PGP)y_{j,\infty}\left[1 + \frac{\alpha}{\exp(\Phi/\beta)^{-\xi}}\right] \tag{20}$$

The ventilation correlation coefficient α primarily reflects the magnitude of the fire properties in nonflaming fires (high □ values). The ventilation correlation coefficient ß reflects the magnitude of the fire properties in the transition region between the well-ventilated and ventilation-controlled combustion of the materials. The ventilation correlation coefficient a reflects the range of □ values for the transition region. High value of α is indicative of strong effect of ventilation on the combustion of the materials. High values of ß and ξ are indicative of rapid change of flaming combustion to nonflaming combustion by a small change in the equivalence ratio, such as for the halogenated polymer (e.g., PVC [polyvinylchoride]), for which combustion in normal air itself is unstable.

Equation 20 suggests the following three conditions for the ventilation-controlled combustion of the polymers: (1) for $\Phi >> \beta$, $y_{j,v} = y_{j,\infty}(1 + \alpha)$, (2) for $\Phi << \beta$, $y_{j,v} = y_{j\infty}$, and (3) for $\Phi \approx \beta$, $y_{j,v} \approx y_{j,\infty}(1 + \alpha/2.7)$.

Figures 7 and 8 show the ratios of the CO and smoke PGP values for the ventilation controlled to well-ventilated combustion as functions of the equivalence ratio. With increase in the equivalence ratio, the CO PGP value increases to as high as 60 times the value for the well-ventilated combustion. The smoke PGP value increases to only about 2.6 times the value for the well-ventilated combustion with increase in the equivalence ratio.

Equation 20 provides a relationship to determine PGP values for various fire ventilation conditions. By knowing or predicting the net heat flux for a fire scenario, the generation rates of the products can be calculated from equations 18 and 19.

Preferential Conversion of Carbon in the Material to CO with Decrease in Fire Ventilation

With decrease in fire ventilation during the combustion of the nonhalogenated materials, the preferential conversion of the carbon in the material to CO follows the order: wood (C-H-O aliphatic structure) > PMMA (C-H-O aliphatic structure) > nylon (C-H-O-N aliphatic structure) > PE (polyethylene) (C-H aliphatic linear unsaturated structure) > PP (polypropylene) (C-H aliphatic branched unsaturated structure) > PS (polystyrene) (C-H aro

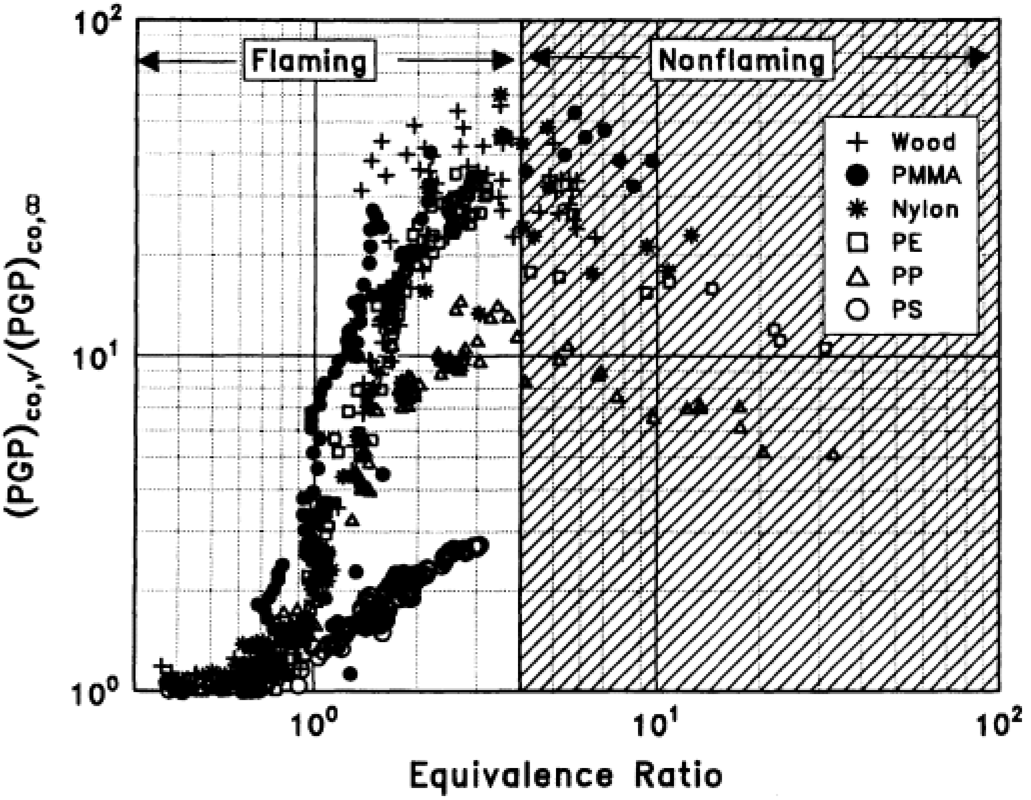

FIGURE 7 Ratio of the CO generation parameter for ventilation-controlled to well-ventilated combustion of materials versus the equivalence ratio.

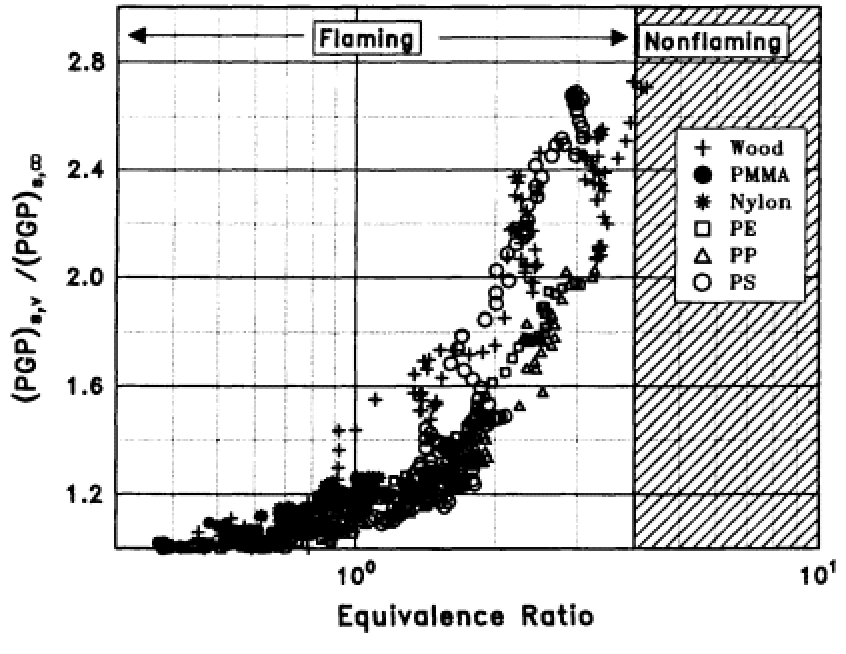

FIGURE 8 Ratio of the smoke generation parameter for ventilation-controlled to well-ventilated combustion of materials versus the equivalence ratio.

matic structure). A similar trend is found for the liquids and gases. The presence of O and N atoms in the chemical structures of the materials with aliphatic C-H structure appears to enhance the preferential carbon atom conversion to CO. The order could be due to preferential pyrolysis of the material to CO and/or preference for the reactions between OH and CO compared to the reactions between OH and C. A decrease in the OH concentration with increase in the equivalence ratio is also suggested by the order.

Preferential Conversion of Carbon in the Material to Smoke with Decrease in Fire Ventilation

With decrease in fire ventilation during the combustion of the nonhalogenated polymers, the preferential conversion of the carbon in the material to smoke follows the order: PS > wood > PE = PP > nylon > PMMA. The order for the preferential conversion of the carbon atom to smoke is opposite to the order for the conversion of the carbon to CO, except for wood. The order could be due to preferential pyrolysis of the material to carbon and/or preference for the reactions between OH and CO compared to the reactions between OH and C, and/or decrease in the concentration of OH.

THERMAL AND NONTHERMAL DAMAGE

Damage due to heat is defined as thermal damage; and damage due to smoke, toxic, and corrosive products is defined as nonthermal damage (Tewarson, 1992). Nonthermal damage depends on the chemical nature and deposition of products on the walls, ceilings, building furnishings, equipment, and components, and so forth, and on the environmental conditions. The severity of the nonthermal damage increases with time. Some examples of nonthermal damage to property are corrosion damage, electrical malfunctions, and damage due to discoloration and odors. Toxic effects of fire products on the human body that result in an injury or loss of life are examples of nonthermal damage to life. The subject of toxicity has been discussed (NRC, 1986). This paper deals with the subject of nonthermal damage in industrial and commercial occupancies due to smoke and corrosive fire products.

The subject of corrosion for commercial and industrial occupancies has been reviewed based on the knowledge derived from the telephone central office (TCO) experience for the deposition of atmospheric pollutants and fire products on equipment, severity of corrosion damage, and ease of cleaning the equipment (Reagor, 1992; FCC, 1993).

In TCO fires involving PVC-based electrical cables, contamination levels in the range of about 5 $\mu g/cm^2$ to 900 $\mu g/cm^2$ have been observed (Reagor, 1992; FCC, 1993). In general, an electronic switch would be expected to accumulate zinc chloride levels in the range of about 5 $\mu g/cm^2$ to 9 $\mu g/cm^2$ from the interaction with the environment over its expected lifetime of 20 or more years. Clean equipment is expected to have less than about 2 $\mu g/cm^2$ of chloride contamination; whereas, contaminated equipment can have as high as 900 $\mu g/cm^2$. Thus, equipment contamination levels due to chloride ions and ease of restoration have been classified into four levels (Reagor, 1992), which are listed in Table 8.

TABLE 8 Contamination Levels for the Surface Deposition of Chloride Ions for Electronic Equipment

Chloride Ion (μg/cm²)	Level	Damage/Cleaning/Restoration
2	One	No damage expected. No cleaning and restoration required.
< 30	Two	Equipment can be easily restored to service by cleaning without little impact on long-term reliability
30 to 90	Three	Equipment can be restored to service by cleaning, as long as no unusual corrosion problems arise, and the environment is strictly controlled soon after the fire.
< 90	Four	The effectiveness of cleaning the equipment dwindles and the cost of cleaning quickly approaches the replacement cost. Equipment contaminated with high chloride levels may require severe environmental controls even after cleaning in order to provide potentially long-term reliable operation.

SOURCE: Data from Reagor (1992).

CORROSION

Corrosion is defined as an unwanted chemical reaction and/or destruction or deterioration of a material because of reaction with its environment. Most of the knowledge on corrosion damage has been based on air pollution, for example, that due to acid rain, and on laboratory scale pyrolysis and combustion experiments.

In fires metal surfaces are exposed to fire products that include water (generated in the combustion process and present in the ambient air). The exposure is of short duration, a few minutes to a few days. Figure 9 shows an example of corrosion of a thin copper film (5,000 A) exposed to the combustion products of PVC homopolymer and commercial materials as measured in the FMRC Flammability Apparatus (Figure 1). The slopes of the lines represent the corrosion rate. The corrosion rate from the PVC homopolymer is significantly higher than the rate from the PVC commercial materials, indicating dilution and/or partial neutralization of hydrogen chloride (HCl) by the pyrolysis products of nonhalogenated additives in commercial materials. The corrosion is faster in the initial stages and becomes slower in later stages due to protective oxide film formation on the surface.

The corrosion rate of a metal exposed to the pyrolysis and combustion products is found to satisfy the following relationship (Tewarson, 1994):

$$\dot{R}_{corr} = \mu c_{corr} \qquad (21)$$

where $\dot{R}_{corr}$ is the corrosion rate (Å/min), μ is corrosion constant [(Å/min)/(kg/m³)], and c_{corr} is the average concentration of the corrosive product (kg/m^3). In the gas phase the average concentration of the corrosive product is equal to the ratio of the total mass of the product in kg to the total volume of water in the gas phase in m^3.

$$\dot{R}_{corr} = \mu C_{corr} \quad (21)$$

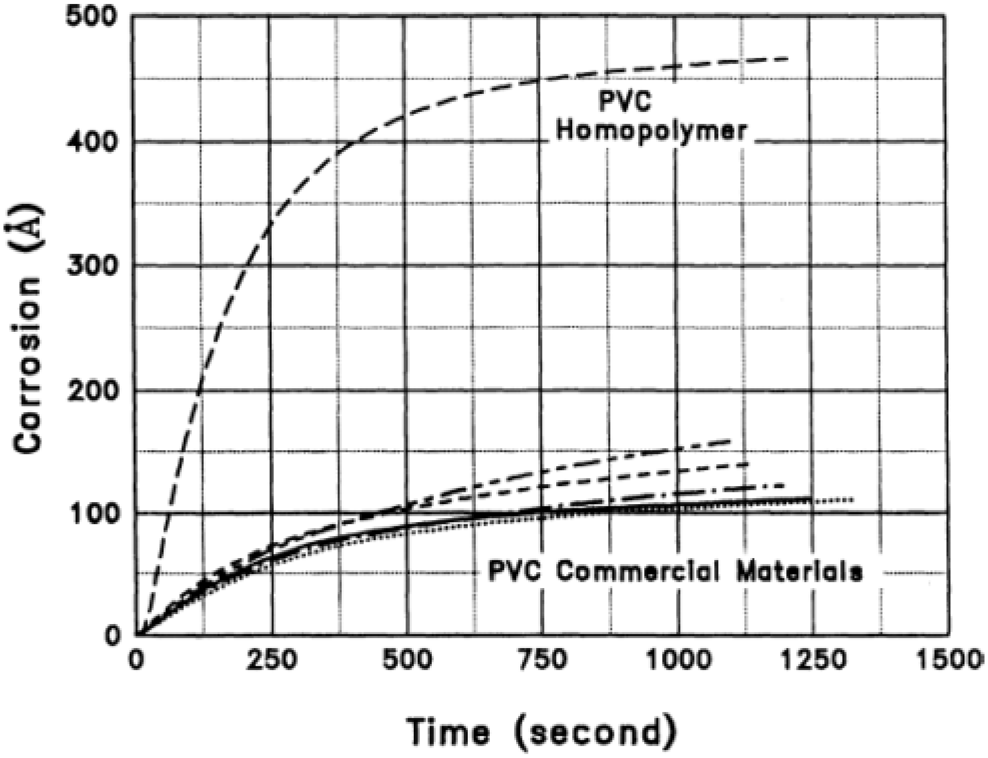

FIGURE 9 Gas-phase corrosion from the combustion products of PVC homopolymer and commercial materials. Data from the FMRC Flammability Apparatus.

The total mass of the corrosive product is equal to $y_{corr}W_T$, where y_{corr} is the yield of the corrosive product (kg/kg) and W_T is the total mass of the material pyrolyzed (kg). If V_T is the total volume of the fire product-air mixture, then the volume of water is f_wV_T, where f_w is the volume fraction of water in the fire product-air mixture. The concentration of the corrosive product then becomes $y_{corr}W_T/ f_wV_T$ and from Equation 21:

$$\dot{R}_{corr} = \frac{\mu y_{corr} W_T}{f_w V_T} \quad (22)$$

Rearranging Equation 22:

$$Corrosion\ Index = \frac{\mu y_{corr}}{F_w} = \dot{R}_{corr}/(W_T/V_T) \quad (23)$$

The corrosion index (CI) is the rate of corrosion per unit average mass concentration of the material pyrolyzed (Å/min)/(kg/m³). The CI values have been reported (Tewarson, 1994). The typical CI value for gas-phase corrosion for a highly halogenated polymer with hydrogen atoms in the structure, such as PVC, is 4 x 10^3 (A/min)/(kg/m^3). For a highly halogenated polymer with no hydrogen atoms in the structure, such as tetrafluoroethylene (TFE), the CI value is 0.6 x 10^3 (Å/min)/(kg/m^3), indicating the importance of the formation of water in the combustion and the inefficiency of the hydrolysis process with water from the ambient air to generate acids.

The CI values suggest that:

- For significant gas-phase corrosion it is necessary to have hydrogen atoms in the structure of the halogenated polymers. For example, the CI values for PVC (hydrogen atoms in the structure) and TFE (no hydrogen atoms in structure) differ by factor of seven. The difference is probably due to (1) the inefficiency of the hydrolysis process in the gas phase during the conversion of fluorocarbon products generated from TFE to hydrogenfluoride; and (2) the high water solubility of hydrogen chloride generated from PVC.
- Fire retardation of nonhalogenated polymers by halogenated compounds increases the CI values.
- Presence of water in the environment is not necessary for the gas-phase corrosion from the products of halogenated polymers with hydrogen atom in the structure as water is generated in the combustion process.
- Increase in the oxygen concentration of the environment increases the CI values.

Fire-hardening requires that within each fire-propagation group, the CI be reduced to values as low as possible.

SMOKE DAMAGE

Smoke is a mixture of black carbon (soot) and aerosol (Siegla and Smith, 1981; Goldberg, 1985). It has been suggested that soot nucleation and growth occur near the highly ionized regions of the flames in combustion processes and that some of the charges are transferred to smoke particles.

Smoke damage in industrial and commercial occupancies is considered in terms of discoloration and odor of the property exposed to smoke; interference in the electric conduction path and corrosion of the parts exposed to smoke is a carrier of the corrosive products.

FLAME EXTINCTION

Flame extinction is achieved by applying fire extinguishing agents, such as water, Halon®, or alternates, which interrupt the pyrolysis, combustion, and fire-propagation processes by: (1) interacting with the burning material in the solid phase (mainly removal of heat), (2) reducing the availability of oxygen to the fire (creation of nonflammable mixture), and (3) removing the heat from the flame and interfering with the chemical reactions within the flame.

The flame extinction requirements are lower for materials with a higher degree of fire-hardening. For example, group N-1 materials with FPI £ 7 do not require fire protection.

When the extinguishing agents, active in the gas phase, are applied to a flame, the HRP values decrease; the PGP values of the products of incomplete combustion, such as CO, smoke, and, mixture of hydrocarbons, increase. These results are very similar to the results for the ventilation-controlled fires (figures 6-8). Figures 10 and 11 show the ratios of the HRP and PGP values for well-ventilated combustion of a polyester-70 percent glass composite system in the presence and absence of Halon® 1301.

In Figure 10, the PGP ratio for hydrocarbons increases to 115, for CO it increases to 10, and for smoke it increases to 2. These results suggest a possible interruption by Halon® 1301 of the reaction(s) in which CO and hydrocarbons are consumed, rather than the reactions in which smoke is consumed. This type of behavior is also found for the ventilation-controlled combustion of materials with oxygen atoms in the structure (figures 7 and 8).

As shown in Figure 11, the HRP ratio decreases to 0.58, below which the flame becomes unstable, leading to flame extinction. This is similar to the behavior shown in Figure 6, which results from the increase of the equivalence ratio.

SUMMARY

Fire-hardened materials offer resistance to pyrolysis, ignition, combustion, and fire propagation and would be materials of choice for commercial aircraft interiors to reduce hazards due to heat (thermal hazard) and smoke, toxic, and corrosive products (nonthermal hazard).

The resistance to pyrolysis and ignition would be increased by increasing the values of (1) the gasification temperature or surface re-radiation loss and heat of gasification to reduce the mass pyrolysis rate, and (2) the ignition temperature or the *critical heat flux* (CHF) and the *thermal response parameter* (TRP) to delay ignition and increase removal of heat from the surface to the interior. Stronger chemical bonds, pyrolysis mechanisms favoring retention of carbon in the solid phase (charring), enhancement of thermal conductivity, density, and specific heat of the materials are some of the factors expected to be effective in this endeavor. Some of the commercial materials introduced recently satisfy these requirements.

The resistance to combustion would be enhanced for materials with high resistance to pyrolysis and ignition. In addition, *the flame heat flux transferred back to the surface and the heat of combustion* need to be decreased to reduce the mass pyrolysis rate in the combustion and the heat release rate. These two fire properties could be reduced by (1) modification of the pyrolysis behavior to enhance release of higher monomer fraction relative to the oligomer fraction, (2) reduction in the carbon atom fraction relative to other atoms in the pyrolysis products (enhancing the char formation), (3) introduction of the oxygen atoms in the structure, and (4) decrease in the chemical bond unsaturation, aromaticity, and others.

Initially the processes of pyrolysis, ignition, and combustion occur within the area where the material is heated. The area is defined as the ignition zone. If the heat flux transferred beyond the ignition zone satisfies the CHF and TRP values, fire propagation beyond the ignition would be initiated. The thermal and nonthermal hazards depend on the rate and extent of fire propagation beyond the ignition zone and are characterized by the *fire-propagation index* (FPI).

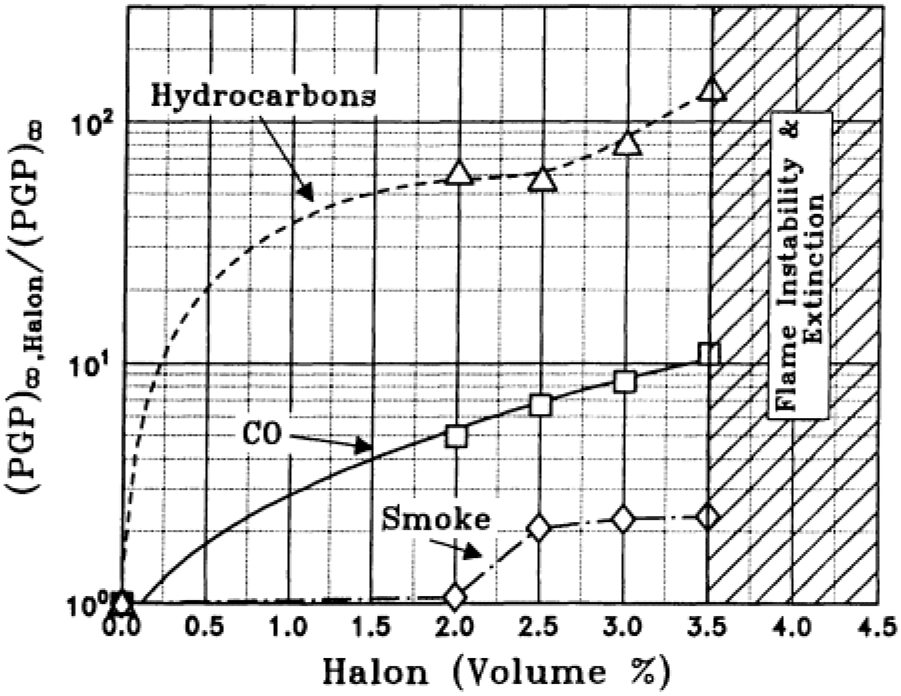

FIGURE 10 Ratio of the PGP in the presence and absence of Halon® 1301 for the well-ventilated combustion of polyester-70 percent glass composite system exposed to 60 kW/m² of external heat flux. Data are from the FMRC Flammability Apparatus.

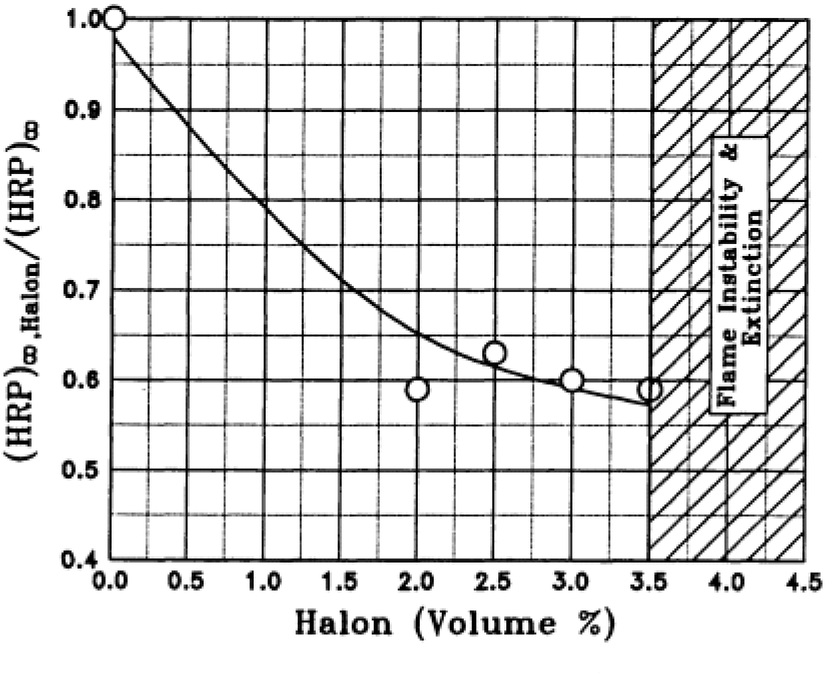

FIGURE 11 Ratio of the HRP in the presence and absence of Halon® 1301 for the well-ventilated combustion of polyester-70 percent glass composite system exposed to 60 kW/m² of external heat flux. Data are from the FMRC Flammability Apparatus.

Under high flame-radiation conditions, that is, large-scale fires, materials with FPI values ≤7 are nonpropagating, group N-1 materials. Materials with FPI values > 7 and < 10 show decelerating propagation and are identified as group D-1 materials. Materials with FPI values ≥ 10, but < 20, show slowly propagating fire beyond the ignition zone and are identified as group P-2 materials. Materials with FPI values ^{3}20 show rapidly propagating fire beyond the ignition zone and are identified as group P-3 materials.

Fire-hardening requires materials to be group N-1 materials. The FPI values would be reduced by increasing the CHF and TRP values and decreasing the heat release rate. Within each fire-propagation group, it is necessary that the heat release rate and the generation rates of fire products be reduced to values as low as possible. The heat release rate within each fire-propagation group is characterized by the *heat release parameter (HRP) (or the ratio of the heat of combustion to heat of gasification).* For group N-1 materials, HRP is ≤2. The generation rates of products within each fire-propagation group are characterized by the *product generation parameter* (PGP) *(or the ratio of the yield of the product to heat of gasification).* The PGP values within each fire-propagation group need to be reduced to as low values as possible. Parameters to characterize smoke and toxic damage have not been defined; for corrosion damage, a *corrosion index* (CI) has been identified as the corrosion rate of a metal per unit concentration of the material pyrolyzed.

NOMENCLATURE

CHF	critical heat flux (kW/m^2)
c_{corr}	average concentration of a corrosive product (kg/m^3)
CI	corrosion index
c_p	specific heat (MJ/kg•K)
ETFE	ethylenetetrafluoroethylene (Tefzel)
f_w	volume fraction water (-)
FG	fiberglass reinforced
FEP	fluorinated ethylene-propylene (Teflon)
FPI	fire propagation index $\{1000\ (0.42\ \dot{Q}'_{cb})^{1/3} / [\Delta T_{ig}\ (kpc_p)^{1/2}]\}$
$\dot{G}''_j$	mass generation rate of product j (kg/m^2•s)
ΔH_i	heat of combustion, gasification, melting, or vaporization per unit mass of material pyrolyzed (MJ/kg)
HRP	heat release parameter ($\Delta H_{cb}/\Delta H_g$)
k	thermal conductivity (kW/m•K)
$\dot{m}_{air}$	mass flow rate of air (kg/s)
$\dot{m}''_p$	mass pyrolysis rate (kg/m^2•s)
M	molecular weight (kg/mole)
PE	polyethylene
PGP	product generation parameter ($y_j/\Delta H_g$)(kg/MJ)
PMMA	polymethylmethacrylate
PP	polypropylene
PS	polystyrene

PVC	polyvinylchloride
$\dot{q}''$	heat flux (kW/m^2)
$\dot{Q}''_i$	heat release rate per unit sample surface area ($\dot{m}''\Delta H_{ch}$) (kW/m^2)
$\dot{Q}'_i$	heat release rate per unit sample width (kW/m)
$\dot{Q}_{corr}$	corrosion rate (Å/min)
S	stoichiometric mass air-to-fuel ratio (-)
t	time (s)
T	temperature (K)
ΔT_{ig}	ignition temperature above ambient (K)
TRP	thermal response parameter, thermally thick $[\Delta T_{ig} (k\rho c_p)^{1/2}]$ $(kW \cdot s^{1/2}/m^2)$
TRP	thermal response parameter, thermally thin $(\Delta T_{ig}\ \delta\rho c_p)$ (kJ/m^2)
u	fire-propagation rate (m/s)
vg	co-flow air velocity (m/s)
V_T	total volume of fire product–air mixture (m^3)
W_T	total mass of material pyrolyzed (kg)
y_j	yield of product j (W_j/W_f) (kg/kg)
Y_o	mass fraction of oxygen (-)

Greek

α	ventilation correlation coefficient for nonflaming region (-)
β	ventilation correlation coefficient for transition region (-)
ξ	ventilation correlation coefficient for the equivalence ratio (-)
Φ	equivalence ratio ($S\dot{m}''_p A/\dot{m}_{air}$)
δ	thickness or depth (m)
δ_f	effective flame heat transfer distance (m)
χ_{ch}	combustion efficiency ($\dot{Q}''_{ch}$ / $\dot{m}''\Delta H_T$)
χ_{con}	convective component of the combustion efficiency ($\dot{Q}''_{con}$ /$\dot{m}''\Delta H_T$) (-)
χ_{rad}	radiative component of the combustion efficiency ($\dot{Q}''_{rad}$ /$\dot{m}''\Delta H_T$) (-)
η_j	generation or consumption efficiency of a product (y_j / Ψ_j) (-)
μ	corrosion constant (Å/min)(kg/m^3)
ρ	density (kg/m^3)
Ψ_j	stoichiometric yield for the maximum conversion of fuel to product j (-)

Subscript

a	air or ambient
ch	chemical
con	convective
corr	corrosion
cr	critical
e	external
f	flame
fc	flame convective
fr	flame radiative
g	gas or gasification

i	chemical, convective, radiative
ig	ignition
j	fire product
m	melting
n	net
o	initial
rad	radiation
stoich	stoichiometric for the maximum possible conversion of the fuel to the product
rr	surface re-radiation
s	surface
th	depth
v	ventilation-controlled fire
w	water
∞	well-ventilated

Superscript

.	per unit time (s^{-1})
'	per unit width (m^{-1})
"	per unit area (m^{-2})

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Fire-Screening Results of Polymers and Composites

Usman Sorathia and C. Beck[*]

ABSTRACT

Fire-screening tests performed by the U.S. Navy in the course of evaluating composite materials are summarized and the relative flammability characteristics of conventional and advanced fiber-reinforced thermoset and thermoplastic composite materials are discussed.

The use of composites inside naval submarines is now covered by MIL-STD-2031 (SH), Fire and Toxicity Test Methods and Qualification Procedure for Composite Material Systems Used in Hull, Machinery, and Structural Applications Inside Naval Submarines. This military standard contains test methods and requirements for flammability characteristics such as flame spread index (ASTM E-162); specific optical density of smoke (ASTM E-662); combustion gas generation, heat release, and ignitability as measured by cone calorimeter (ASTM E-1354); oxygen-temperature index; and long-term outgassing. Over the past 5-7 years, the Carderock Division of the Naval Surface Warfare Center (CDNSWC) has evaluated commercially available and developmental polymers and composites for flammability characteristics, with particular emphasis on heat release rates and ignitability (time to ignition) as determined by cone calorimetry. This paper presents the summary of relative flammability characteristics of conventional and advanced fiber-reinforced, organic matrix thermoset and thermoplastic composite materials suitable for surface ship and submarine applications. The thermoset materials evaluated included vinyl esters (VE), epoxies (EP), cyanate ester (CE), bismaleimides (BMI), phenolics (PH), and polyimides (PI). Thermoplastic materials evaluated included polyphenylene sulfide (PPS), polyethersulfone, polyarylsulfone, polyetheretherketone (PEEK), and polyetherketoneketone (PEKK).

INTRODUCTION

The introduction of composite materials into both the marine and aerospace industries began during the 1940s with the use of polyesters as the primary matrix material. Today, aerospace and aircraft use of composites relies heavily on graphite-reinforced epoxy and high glass transition temperature bismaleimide resins to provide optimum mechanical properties at much reduced weight, and on glass-reinforced phenolic and other thermoplastic materials for interior applications to meet Federal Aviation Requirements (FAR) fire-worthiness criteria. Aircraft and aerospace industries have successfully used the composite materials now for over 25 years. This is due to the premium placed on weight savings in the aircraft business. Current seaborne applications of composite materials in the U.S. Navy have been limited. For submarines, these applications include sonar bow domes and windows, towed array fairings, and

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prototype diving plane and control surfaces. The focus for surface ships has been on coastal minehunter (MHC-51) hulls (Gagorik et al., 1991). Over the past 10 years, however, there has been a growing interest in the development and application of composites for both primary and secondary load-bearing structures such as foundation, deckhouses, and hulls; for machinery components such as composite piping, valves, centrifugal pumps, and heat exchangers; and for auxiliary or support items such as gratings, stanchions, ventilation ducts, and screens (Caplan, 1993). This new interest in composite materials is due to increased need for a corrosion-free, lightweight, and affordable low-cost alternative to metallic components. A significant technical issue that has limited composite use on board naval ships and submarines is the combustible nature, and hence the fire, smoke, and toxicity, of organic matrix composite materials.

The use of structural composites inside naval submarines is now covered by MIL-STD2031 (SH), Fire and Toxicity Test Methods and Qualification Procedure for Composite Material Systems Used in Hull, Machinery, and Structural Applications Inside Naval Submarines (DOD, 1991). Fire testing specified in this standard is intended to support hazard analyses of the composites for proposed application. The approach philosophy (DeMarco, 1991) taken by the Navy in the development of MIL-STD-2031 (SH) centered on determining the types of fires that could occur, understanding the potential threat from a fire, and determining the bounds of that threat so that performance criteria could be established. It was also established that a sufficient range of material fire testing would be required to understand the performance of composite system and to permit a risk-benefit assessment.

Two guiding criteria were established for the use of composite systems aboard naval vessels: (1) The composite system will not be the fire source, that is, it will be sufficiently fire-resistant not to be a source of spontaneous combustion. (2) Secondary ignition of the composite system will be delayed until the crew can respond to the primary fire source, that is, the composite system will not result in rapid spreading of the fire.

This military standard is significantly more stringent than FAR 25.853, which regulates the materials used for aircraft interiors on the basis of, among other things, flame spread, smoke emission, and heat release rate. The Navy requires the use of ASTM E-1354 (heat release rate using an oxygen consumption calorimeter) to measure heat release rates and ignitability at four different fluxes of 25, 50, 75, and 100 kW/m². FAR mandates OSU (Ohio State University) apparatus at one heat flux of 35 kW/m² to measure peak heat release rate, and total heat release for the first 2-minute duration, the requirement for aircraft certification being 65/65. In addition, the Navy requires the ignitability tests, the requirement being 300, 150, 90, and 60 seconds at 25, 50, 75, and 100 kW/m², respectively. The Navy requires smoke emission (E-662) of no more than 100 for the first 5-minute duration, whereas FAR requires smoke emission of no more than 200 for the first 4 minutes. The Navy requires the flame spread index (E-162) of 20 or less whereas FAR requires the traditional Bunsen burner test. Table 1 summarizes the requirements of MIL-STD-2031.

The Navy currently has no specific standard for surface ships. The flammability requirements for surface ships are different from those for submarines. Instead of survivability measured in minutes, as it is in submarine fires, the critical issue in surface ship fires is the residual strength of structures at elevated temperatures for a period of 30-60 minutes.

During the past decade, the introduction of new or modified resins in both the thermoset and thermoplastic family of polymers has resulted in steady improvement in the upper temperature limits, and hence their thermal stability. The upward temperature limits have also improved fire and smoke properties of these new state-of-the-art polymers and offer the potential of improved fire-resistant composite materials. **For** the past several years, CDNSWC, Annapolis Detachment (formerly known as DTRC), has been evaluating the fire performance of commercially available and developmental composite materials under the 6.2 Materials Block Program sponsored by the Office of Naval Technology. This program also included work on thermal barriers to protect the composite structures against fire damage (Sorathia et al., 1992a, b). This paper summarizes small-scale fire performance characteristics of selected state-of-the-art and conventional composite materials and assesses the suitability of these materials for use inside naval submarines. Table 2 lists the composite materials evaluated at CDNSWC and discussed

TABLE 1 Summary of Test Methods and Requirements, MIL-STD-2031

Fire Test/ Characteristic	Requirement	Test Method	Oxygen-temperature index	Minimum	ASTM D-2863 Modified
% oxygen at 25 °C	35				
% oxygen at 75 °C	30				
% oxygen at 300 °C	21				
flame spread index	20 (maximum)	ASTM E-162			
Ignitability (s)	Minimum	ASTM E-1354			
100 kW/m^2 irradiance	60				
75 kW/m^2 irradiance	90				
50 kW/m^2 irradiance	150				
25 kW/m^2 irradiance	300				
Heat release (kW/m^2)	Maximum	ASTM E-1354			
100 kW/m^2 irradiance, peak	150				
Average for 300 s	120				
75 kW/m^2 irradiance, peak	100				
Average for 300 s	100				
50 kW/m^2 irradiance, peak	65				
Average for 300 s	50				
25 kW/m^2 irradiance, peak	50				
Average for 300 s	50				
Smoke obscuration	Maximum	ASTM E-662			
D8 during 300 s	100				
Dmax	200				
Combustion gas generation	CO = 200 ppm	ASTM E-1354			
(25 kW/m^2)	CO_2 = 4%v HCN = 30 ppm HCl = 100 ppm				
N-Gas model smoke toxicity	No deaths	Modified			
Screening test	Pass	NBSTTM			

in this paper. All composite systems have a thickness of approximately 0.175-0.250 inches unless mentioned otherwise.

FIRE PERFORMANCE OF COMPOSITE LAMINATES

The fire performance of composite materials are those characteristics that describe the response of polymeric materials when exposed to fire (Hilado, 1982). These include flame spread (fire propagation), smoke evolution (visibility), combustion gas generation (toxicity), fire endurance (residual strength during and after fire exposure), heat release and ignitability (fire growth), and ease of extinguishment (oxygen index). The following sections explain some of the tests used to assess these properties and the results obtained from these tests.

Flame-Spread Index (ASTM E-162)

Flame spread has been defined as the progress of flame over a surface. It is used to describe the response of materials to heat and flame under controlled laboratory conditions. The rate at which flame will travel along surfaces depends upon the physical and thermal properties of the material, its method of mounting and orientation, type and level of fire or heat exposure, the availability of air, and properties of the surrounding enclosure. The standard radiant panel test procedure for surface flammability is ASTM E-162. The threat consideration tested in the flame spread test is that a fire will be controllable in 300 seconds, thereby providing time for active extinguishment efforts.

This method uses an inclined 6 x 18 in. panel in front of which a radiant heat source (670 °C or 1238 °F) is placed. A pilot flame, located at the upper edge of the test specimen, ignites the specimen. The orientation of the specimen is such that ignition is forced near its upper edge and the flame front progresses downward. A factor derived from the rate of progress of the flame front and another relating to the rate of heat liberation by the material under test are combined to provide flame spread index.

Table 3 lists the flame spread index of many composite materials evaluated at CDNSWC. As shown, autoclaved cured epoxies, bismaleimides, phenolics, polyimides, and advanced thermoplastics all have low flame spread characteristics (under 20). Polyethylene and aramidreinforced phenolic composites had high flame spread index due to the combustible nature of polymeric fibers.

Smoke and Combustion Gas Generation (ASTM E-662)

Smoke is defined as the visible, nonluminous, airborne suspension of particles originating from a combustion process. Smoke affects visibility and hinders the ability of the occupants to escape and of fire fighters to locate and suppress the fire. Smoke density is influenced by the degree of ventilation.

TABLE 2 Summary of Composite Materials Evaluated at Carderock Division, Naval Surface Warfare Center

Composite	Identification
Glass/VE (1031)	Glass/vinyl ester, fire retardant, brominated
Glass/VE (1087)	Glass/vinyl ester, non-fire-retardant
Glass/epoxy (1089)	Glass/epoxy, S2/3501-6, (0/90),
Glass/epoxy (1066)	Glass/epoxy, 105/206, RT cure, post-cured
Glass/epoxy (1067)	Glass/epoxy, 125/226, RT cure, post-cured
Glass/epoxy (1040)	Glass/epoxy, E-Glass/F155
Glass epoxy (1071)	Glass/epoxy, S2/F155
Glass/epoxy (1006)	Glass/epoxy, 7701/7781
Glass/epoxy (1070)	Sonar bow dome, MXB7780/3783
Glass/epoxy (1003)	RTM, 9405/9470
Glass/epoxy (1090)	SL-851-H4, SMC, 50% glass
Graphite/epoxy (1091)	T-300/5208, (0/90),, 350 °F
Graphite/epoxy (1092)	AS4/LC1, anhydride-cured
Graphite/epoxy (1093)	Graphite/epoxy, AS4/3501-6
Graphite/epoxy (1094)	P55/ERLX, toughened epoxy
Glass/CE (1046)	Glass/cyanate ester
Graphite/M.BMI (1095)	T300/5245C, modified bismaleimide
Glass/BMI (1096)	T2E225/F650
Graphite/BMI (1097)	T6T145/F650, (0/90),, Post-cured at 475 ºF for 4 hr.
Graphite/BMI (1106)	T6T145/F655, toughened
Graphite/BMI (1098)	Compimide HTA-7/65FWR
Glass/phenolic (1014)	J2027/Phencat 10, RT cure, PC at 140 °F/6 hr.
Glass/phenolic (1015)	Mark IV, RT cure, PC at 140 °F/6 hr.
Glass/phenolic (1017)	Fire PRF2, RT cure, PC at 140 °F/6 hr.
Glass/phenolic (1018)	350D66 RT cure, PC at 140 °F/6 hr.
Glass/phenolic (1099)	Q6399, developmental RT-curing phenolic system
Glass/phenolic (1100)	CPH 2265/7781, cure at 250 ºF.
Glass/phenolic (1101)	CPH 2265/7781, post-cured at 350 °F
Graphite/phenolic (1102)	3C584/F453-1, structural, heat resistant
Graphite/phenolic (1103)	R1620, toughened, structural
Graphite/phenolic (1104)	402/7781
PE/phenolic (1073)	Polyethylene fibers 1000, 985PT/Mark IV
Aramid/phenolic (1074)	Aramid fibers 49, 900-F1000/Mark IV
Glass/polyimide (1105)	CPI 2237/6781, PMR-15 polyimide system
Graphite/PNi (1080)	Graphite/phthalonitrile, NRL
Glass/PP (1082)	Glass/polypropylene
Glass/J-2 (1077)	Glass/nylon
Glass/PPS (1069)	AG 40-70, polyphenylene sulfide
Graphite/PPS (1083)	AC 40-60, polyphenylene sulfide
Glass/PPS (1084)	LG 40-70, polyphenylene sulfide
Graphite/PPS (1085)	LC 31-60, T300, polyphenylene sulfide
Graphite/PAS (1081)	T650-42/Radel X, polyarylsulfone
Graphite/PES (1078)	4084/PES-1, IM8/ITA
Graphite/PEEK (1086)	APC-2/AS4, polyetheretherketone
Glass/PEKK (1079)	S2/PEKK, polyetherketoneketone

TABLE 3 Flame Spread Index (ASTM E-162)

Composite	Index
Glass/VE (1087)	156
Glass/VE (1031)	27
Glass/epoxy (1066)	43
Glass/epoxy (1067)	12
Glass/epoxy (1089)	11
Glass/epoxy (1091)	11
Glass/epoxy (1092)	23
Graphite/M.BMI (1095)	13
Glass/BMI (1096)	17
Graphite/BMI (1097)	12
Graphite/BMI (1098)	3
Glass/phenolic (1099)	1
Glass/phenolic (1100)	5
Glass/phenolic (1101)	4
Glass/phenolic (1014)	4
Glass/phenolic (1015)	4
Glass/phenolic (1017)	6
Glass/phenolic (1018)	4
Graphite/phenolic (1102)	6
Graphite/phenolic (1103)	20
Graphite/phenolic (1104)	3
PE/phenolic (1073)	48
Aramid/phenolic (1074)	30
Glass/polyimide (1105)	2
Glass/J-2 (1077)	13
Glass/PPS (1069)	7
Graphite/PPS (1083)	3
Glass/PPS (1084)	8
Graphite/PPS (1085)	3
Graphite/PAS (1081)	9
Graphite/PEEK (1086)	3
Glass/PEKK (1079)	3

Test method ASTM E-662 covers the determination of specific optical density of smoke generated by solid materials. Measurement is made of the attenuation of a light beam by smoke accumulating within a closed chamber due to nonflaming pyrolytic decomposition and flaming combustion. Measurements made with the test relate to light transmission through smoke and are similar to the optical density scale for human vision.

Combustion gas generation is defined as the gases evolved from materials during the process of combustion. The most common of gases evolved during combustion are carbon monoxide (CO) and carbon dioxide (CO_2), along with hydrogen chloride (HCl), hydrogen cyanide (HCN), and others, depending upon the matrix resin chemistry of a given composite material. The Committee on Fire Toxicology of the National Research Council has concluded that as a basis for judging or regulating materials performance in a fire, combustion product toxicity data must be used only within the context of fire hazard assessment. The committee believed that required smoke toxicity was best obtained with animal exposure methods for purposes of predicting the fire hazard of different materials (NRC, 1986).

Table 4 presents smoke density and the relative concentrations of combustion gas generation (Draeger colorimetric tube) in flaming mode during smoke obscuration test (ASTM E-662) for several composite materials. Figure 1 shows the maximum specific optical density and specific optical density at 300 seconds for selected composite systems in flaming mode only. With the exception of vinyl ester, all other composite systems had the specific optical density at 300 seconds of less than 100. Of the thermosets, glass- or graphite-reinforced phenolic composites have very low-smoke. This is also true for all advanced thermoplastics, which also have low maximum smoke density. In general, thermoset composite materials give off more carbon monoxide than thermoplastic composites. One interesting observation was that thermoplastic panels evaluated in this study had slightly expanded or foamed up in the middle during smoke density tests, presumably due to the gases escaping through the softened front face during fire exposure. This may translate into greater structural damage or loss during fire exposure.

Residual Flexural Strength (ASTM D-790)

Flexural strength was selected to characterize the residual mechanical integrity of composite panels after fire exposure. As part of the testing protocol, all specimens (3 x 3 in.) were exposed at radiant heat source of 25 kW/m² for a duration of 20 minutes during ASTM E662 in a flaming mode. The specimens were reclaimed and cut into 1/2 x 3 in. coupons, each specimen yielding five coupons. These coupons were tested in accordance with ASTM D-790 using a universal testing machine. Specimens were tested for flexural strength before and after the fire test. Comparison of selected composites on the basis of percentage residual flexural strength retained after the fire exposure is shown in Table 5.

As shown, graphite/PEEK exhibited the maximum flexural strength retained (75 percent) at this level of fire exposure. Insofar as thermoplastics soften during heating, measurements of flexural strength retained after fire testing may not give true or accurate flexural properties during fire. What is needed is the real-time measurement of flexural integrity of composite structures during exposure to fire. The measurement, analytical prediction, and validation of structural integrity during and after fire exposure is being vigorously pursued by CDNSWC, the University of Washington, and the University of Maryland (Milke and Vizzini, 1991; Ritter et al., 1992; Sorathia et al., 1993).

Heat Release and Ignitability (ASTM E-1354)

Heat release is defined as the heat generated in a fire due to various chemical reactions occurring within a given weight or volume of material. The major contributors are those reactions where carbon monoxide and carbon dioxide are generated and oxygen is consumed (Tewarson, 1988). Different levels of radiant flux simulate fire scenarios in which the composite material is itself burning or in which it may be near another burning material. Heat release data

TABLE 4 Smoke and Combustion Gas Generation (ASTM E-662)

Composite	D_s (300 s)	D_{max} (ppm)	CO (% v)	CO_2 (ppm)	HCN (ppm)	HCl (ppm)
Glass/VE (1031)	463	576	230	0.3	ND[a]	ND
Glass/VE (1087)	310	325	298	1.5	1	0.5
Glass/epoxy (1089)	56	165	283	1.5	5	ND
Glass/epoxy (1066)	2	408	200	2	5	2
Glass/epoxy (1067)	16	456	250	1	2	ND
Glass/epoxy (1071)	17	348	80	0.5	3	1
Glass/epoxy (1090)	96	155	50	0.2	ND	ND
Graphite/epoxy (1091)	75	191	115	0.9	15	TR[b]
Graphite/epoxy (1092)	66	210	313	2	1	0.5
Graphite/epoxy (1093)	3	353	160	0.5	2	1.5
Graphite/epoxy (1094)	1	301	300	0.6	2	1
Glass/CE (1046)	4	84				
Graphite/M. BMI (1095)	24	158	30	0.3	1	ND
Graphite/BMI (1097)	6	171	175	0.8	3	ND
Graphite/BMI (1098)	9	117	10	TR	TR	1
Glass/BMI (1096)	34	127	300	0.1	7	TR
Glass/phenolic (1100)	4	18	300	1	1	1
Glass/phenolic (1099)	4	43	50	TR	TR	ND
Glass/phenolic (1101)	1	23	300	1	1	1
Glass/phenolic (1014)	1	1	300	1	TR	ND
Glass/phenolic (1015)	1	3	190	1	TR	TR
Glass/phenolic (1017)	1	4	200	1	ND	ND
Glass/phenolic (1018)	1	1	200	1	TR	ND
Graphite/phenolic (1102)	1	24	115	0.5	1	1
Graphite/phenolic (1103)	40	138	100	0.1	1	ND
Graphite/phenolic (1104)	1	4	600	1	2	ND
PE/phenolic (1073)	1	241	700	2	2	ND
Aramid/phenolic (1074)	2	62	700	1.5	2	ND
Glass/polyimide (1105)	1	16	200	1	TR	2
Glass/J-2 (1077)		328	180	1	10	ND
Glass/PPS (1069)	8	87	70	0.5	2	0.5
Graphite/PPS (1083)	2	32	100	0.5	1	ND
Glass/PPS (1084)	4	54	100	1	TR	TR
Graphite/PPS (1085)	1	26	100	1	TR	TR
Graphite/PAS (1081)	2	3	55	0.1	TR	ND
Graphite/PES (1078)	1	5	110	1	1	1
Graphite/PEEK (1086)	1	1	TR	TR	ND	ND
Glass/PEKK (1079)	1	4	200	1	ND	TR

[a] ND: not done.

[b] TR: trace amounts.

provide a relative fire hazard assessment for materials in that materials with low hear release per unit weight or volume will do less damage to the surroundings than the material with high release rate. The rate of heat release, especially the peak amount, is the primary characteristic determining the size, growth, and suppression requirements of a fire environment (Brown et al., 1988).

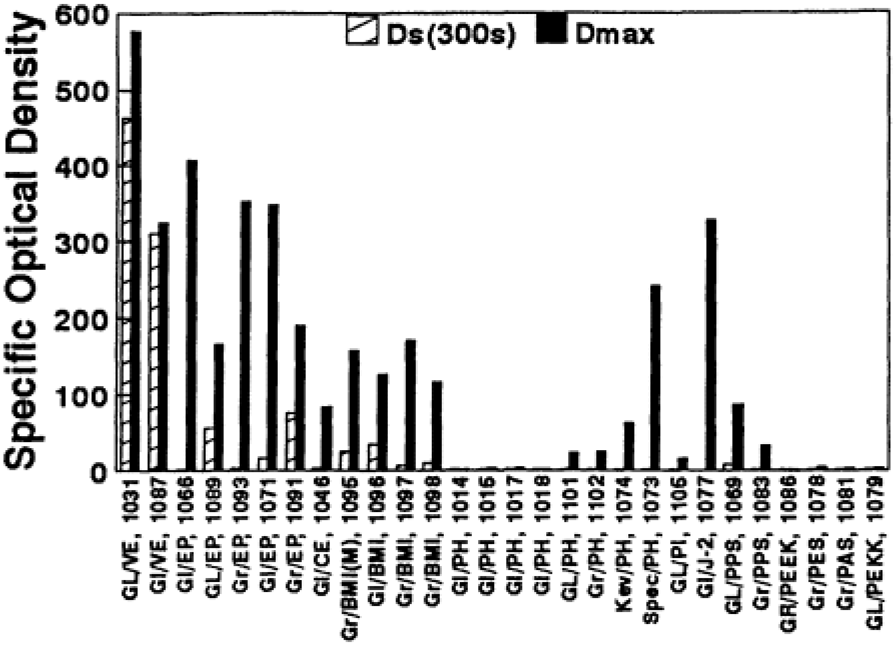

FIGURE 1 Smoke density of selected composites.

TABLE 5 Residual Flexural Strength (ksi) (ASTM D-790)

Composite	Before	After	% Retained
Glass/VE (1087)	54	17	32
Glass/VE (1088)	59	8	14
Glass/epoxy (1089)	168	9	5
Graphite/epoxy (1091)	104	0	0
Graphite/M.BMI (1095)	125	5	4
Glass/BMI (1096)	148	31	21
Graphite/BMI (1097)	115	18	16
Graphite/BMI (1098)	175	24	14
Graphite/phenolic (1102)	54	29	53
Graphite/phenolic (1103)	41	12	30
Glass/polyimide (1105)	114	51	45
Glass/PPS (1085)	47	17	36
Graphite/PPS (1083)	72	29	41
Graphite/PEEK (1086)	144	109	75
Graphite/PAS (1081)	117	39	34

Test method ASTM E-1354 (oxygen consumption cone calorimeter) covers the measurement of the response of materials exposed to controlled levels of radiant heating and is used to determine the heat release rates, ignitability, mass-loss rates, effective heat of combustion, and visible smoke development. These values are becoming increasingly important in determining fire growth and are needed in the various fire models that are being developed. Specific thermal insults of 25, 50, 75, and 100 kW/m² are required. These thermal insults correspond to a small Class A fire, a large trash can fire, a significant fire, and a pool oil fire. The test method utilizes the oxygen consumption principle in which the heat release rate is computed from the measurements of mass flow rate and oxygen depletion in the gas flow.

Table 6 presents heat release and ignitability data on thermoset and thermoplastic composites. Figures 2, 3, and 4 show, respectively, the peak heat release rates, time to ignition, and weight loss (percentage) at 25, 50, 75, and 100 kW/m² for the selected composite material systems. Of all the materials evaluated, phenolics, modified polyimides, and phthalonitrile exhibited the highest resistance to ignition at 100 kW/m². Thermoplastics, in general, exhibited lower heat release rates.

TABLE 6 Heat Release and Ignitability of Composite Materials

Material System	Irradiance (kW/m²)	Weight Loss (%)	Ignitability (s)	Peak Heat Release (kW/m²)	Average Heat Release, 300 s (kW/m²)	Total Heat Release (MJ/m²)	Extinction Area (m²/kg)
Thermosets							
Glass/VE (1031)	25	14	278	75	29	11	1,185
	50	26	74	119	78	25	1,721
	75	29	34	139	80	27	1,791
	100	28	18	166		22	1,899
Glass/VE (1087)	25	36	281	377	180	55	1,188
	50	-	-	-	-		
	75	34	22	499	220	68	1,218
	100	33	11	557		64	1,466
Glass/epoxy (1089)	25	-	535	39	30	10	470
	50	-	105	178	98	30	580
	75	-	60	217	93	28	728
	100	-	40	232	93	24	541
Glass/epoxy (1066)	25	20	140	231	158	52	1,096
	50	23	48	266	154	48	1,055
	75	24	14	271	157	48	1,169
	100	24	9	489	-	46	1,235

Material System	Irradiance (kW/m²)	Weight Loss (%)	Ignitability (s)	Peak Heat Release (kW/m²)	Average Heat Release, 300 s (kW/m²)	Total Heat Release (MJ/m²)	Extinction Area (m²/kg)
Glass/ epoxy (1067)	25	18	209	230	120	41	1,148
	50	20	63	213	127	39	1,061
	75	21	24	300	138	43	1,109
	100	20	18	279	-	32	1,293
Glass/ epoxy (1040)	25	-	-	-	-	-	-
	50	19	18	40	2	29	566
	75	21	13	246	1	38	605
	100	23	9	232	5	47	592
Glass/ epoxy (1071)	25	7	128	20	4	1	1,356
	50	5	34	93	-	3	1,757
	75	23	18	141	99	30	1,553
	100	25	10	202	108	34	1,310
Glass/ epoxy (1006)	25	14	159	81	63	28	2,690
	50	28	49	181	108	39	1,753
	75	24	23	182	-	35	1,917
	100	29	14	229	131	41	1,954
Glass/ epoxy (1070)	25	23	229	175	95	45	1,119
	50	28	63	196	143	49	1,539
	75	27	30	262	133	43	1,440
	100	30	23	284	-	36	1,640
Glass/ epoxy (1003)	25	17	198	159	93	36	1,162
	50	22	50	294	135	43	1,683
	75	22	73	191	121	41	1,341
	100	22	19	335	122	37	1,535
Glass/ epoxy (1090)	25	19	479	118	67	38	643
	50	28	120	114	90	55	803
	75	34	54	144	115	64	821
	100	34	34	173	150	71	1,197

Material System	Irradiance (kW/m²)	Weight Loss (%)	Ignitability (s)	Peak Heat Release (kW/m²)	Average Heat Release, 300 s (kW/m²)	Total Heat Release (MJ/m²)	Extinction Area (m²/kg)
Graphite/ epoxy (1091)	25	7	NI	NI	NI	NI	601
	50	-	-	-	-	-	-
	75	25	53	197	90	30	891
	100	38	28	241	-	28	997
Graphite/ epoxy (1092)	25	-	275	164	99	32	525
	50	-	76	189	116	37	593
	75	-	32	242	112	37	363
	100	-	23	242	113	71	235
Graphite/ epoxy (1093)	25	13	338	105	69	-	-
	50	24	94	171	93	-	-
	75	23	44	244	147	-	-
	100	22	28	202	115	-	-
Glass/CE (1046)	25	8	199	121	74	30	794
	50	22	58	130	71	49	898
	75	23	20	196	116	58	1,023
	100	24	10	226	141	47	1,199
Graphite/ M.BMI (1095)	25	19	237	160	103	32	645
	50	-	-	-	-	-	-
	75	24	42	213	115	36	685
	100	26	22	270	124	38	706
Graphite/ BMI (1097)	25	5	NI	NI	NI	NI	238
	50	-	-	-	-	-	-
	75	30	66	172	130	45	933
	100	31	37	168	130	41	971
Graphite/ BMI (1098)	25	-	NI	NI	NI	NI	NI
	50	13	110	74	51	14	228
	75	15	32	91	65	17	370
	100	16	27	146	75	22	383

Material System	Irradiance (kW/m²)	Weight Loss (%)	Ignitability (s)	Peak Heat Release (kW/m²)	Average Heat Release, 300 s (kW/m²)	Total Heat Release (MJ/m²)	Extinction Area (m²/kg)
Glass/BMI (1096)	25	17	503	128	105	40	324
	50	25	141	176	161	60	546
	75	30	60	245	199	76	604
	100	30	36	285	219	73	816
Glass/ phenolic (1099)	25	-	NI	NI	NI	NI	NI
	50	-	121	66	43	18	4
	75	-	33	102	86	33	85
	100	-	22	122	95	40	-
Glass/ phenolic (1100)	25	-	NI	NI	NI	NI	NI
	50	-	125	66	48	17	308
	75	-	20	120	63	21	365
	100	-	40	163	74	21	441
Glass/ phenolic (1101)	25	-	NI	NI	NI	NI	NI
	50	-	210	47	38	14	176
	75	-	55	57	40	16	161
	100	-	25	96	70	22	620
Glass/ phenolic (1014)	25	-	NI	NI	NI	NI	NI
	50	12	214	81	40	17	83
	75	16	73	97	54	20	246
	100	16	54	133	78	21	378
Glass/ phenolic (1015)	25	-	NI	NI	NI	NI	NI
	50	6	238	82	73	15	75
	75	8	113	76	37	7	98
	100	13	59	80	62	12	58
Glass/ phenolic (1017)	25	-	NI	NI	NI	NI	NI
	50	10	180	190	139	43	71
	75	14	83	115	84	17	161
	100	18	43	141	73	19	133
Glass/ phenolic (1018)	25	-	NI	NI	NI	NI	NI
	50	3	313	132	22	12	143
	75	11	140	56	44	11	74
	100	13	88	68	58	13	66

Material System	Irradiance (kW/m²)	Weight Loss (%)	Ignitability (s)	Peak Heat Release (kW/m²)	Average Heat Release, 300 s (kW/m²)	Total Heat Release (MJ/m²)	Extinction Area (m²/kg)
Graphite/ phenolic (1102)	25	4	NI	NI	NI	NI	NI
	50	-	-	-	-	-	-
	75	28	79	159	80	28	261
	100	-	45	196	-	-	-
Graphite/ phenolic (1103)	25	-	NI	NI	NI	NI	NI
	50	28	104	177	112	50	253
	75	27	34	183	132	50	495
	100	29	20	189	142	51	493
Graphite \phenolic (1104)	25	-	NI	NI	NI	NI	NI
	50	9	187	71	41	14	194
	75	11	88	87	-	11	194
	100	11	65	101	-	11	232
PE/phenolic (1073)	25	30	714	NI	NI	NI	NI
	50	61	129	98	83	107	294
	75	60	28	141	92	104	500
	100	67	10	234	131	96	580
Aramid/ phenolic (1074)	25	4	1,110	NI	NI	NI	NI
	50	43	163	51	40	57	156
	75	40	33	93	54	45	240
	100	65	15	104	72	95	333
Glass/ polyimide (1105)	25	-	NI	NI	NI	NI	NI
	50	11	175	40	27	21	170
	75	13	75	78	49	22	131
	100	14	55	85	60	20	113
Graphite/ PNi (1080)	25	-	-	-	-	-	-
	50	-	-	-	-	-	-
	75	-	-	-	-	-	-
	100	13	75	118	36	12	610

Material System	Irradiance (kW/m²)	Weight Loss (%)	Ignitability (s)	Peak Heat Release (kW/m²)	Average Heat Release, 300 s (kW/m²)	Total Heat Release (MJ/m²)	Extinction Area (m²/kg)
Thermoplastics							
Glass/PP (1082)	25	37	168	187	153	88	702
	50	36	47	361	248	82	959
	75	37	23	484	265	82	1,077
	100	36	13	432	-	82	1,120
Glass/J-2 (1077)	25	-	193	67	38	-	803
	50-	53	96	49	-		911
	75-	21	116	48	-		866
	100	-	13	135	76	-	1,011
Glass/PPS (1069)	25	-	NI	NI	NI	NI	NI
	50	12	105	52	25	32	585
	75	12	57	71	56	24	575
	100	14	30	183	106	41	749
Graphite/PPS (1083)	25	-	NI	NI	NI	NI	NI
	50	-	-		-		-
	75	34	69	81	60	37	431
	100	23	26	141	80	37	752
Glass/PPS (1084)	25	-	NI	NI	-	-	-
	50	13	244	48	28	39	690
	75	15	70	88	67	35	954
	100	16	48	150	94	35	613
Graphite/PPS (1085)	25	-	NI	NI	-	-	-
	50	16	173	94	70	26	604
	75	17	59	66	50	23	-
	100	26	33	126	88	33	559
Graphite/PAS (1081)	25	-	NI	NI	NI	NI	NI
	50	3	122	24	8	1	79
	75	18	40	47	32	14	211
	100	18	19	60	44	14	173

Material System	Irradiance (kW/m²)	Weight Loss (%)	Ignitability (s)	Peak Heat Release (kW/m²)	Average Heat Release, 300 s (kW/m²)	Total Heat Release (MJ/m²)	Extinction Area (m²/kg)
Graphite/ PES (1078)	25	-	NI	NI	NI	NI	NI
	50	-	172	11	6	3	145
	75	-	47	41	23	22	88
	100	-	21	65	39	23	189
Graphite/ PEEK (1086)	25	-	NI	NI	NI	NI	NI
	50	2	307	14	8	3	69
	75	18	80	54	30	35	134
	100	16	42	85	56	28	252
Glass/ PEKK (1079) 25	25	-	NI	NI	NI	NI	NI
	50	6	223	21	10	15	274
	75	10	92	45	24	20	-
	100	6	53	74	46	24	891

Oxygen-Temperature Index

The test method employing oxygen-temperature index is basically the same as ASTM D-2863 for limiting oxygen index but with a series of oxygen index determinations over the temperature range from ambient to 300 ° *C*. Limiting oxygen index is defined as the minimum concentration of oxygen in an oxygen-nitrogen atmosphere necessary to sustain flaming combustion. The purpose of the test is to rank ignitability over a range of temperatures. As the temperature of a material increases, ignition of the material requires less oxygen. Thirty-five percent oxygen is the level above which materials have proven to be good fire performers. Table 7 presents the oxygen index for various thermoset and thermoplastic composites. During fire extinguishment, composites should be cooled below the temperature corresponding to an oxygen index of 21 to prevent re-ignition.

DISCUSSION

Fire performance characteristics of composites are dependent on the chemical nature and amount of the resin matrix used; the type, amount, and orientation of the fiber; additives or modifiers present in the system; and the processing or fabrication techniques employed.

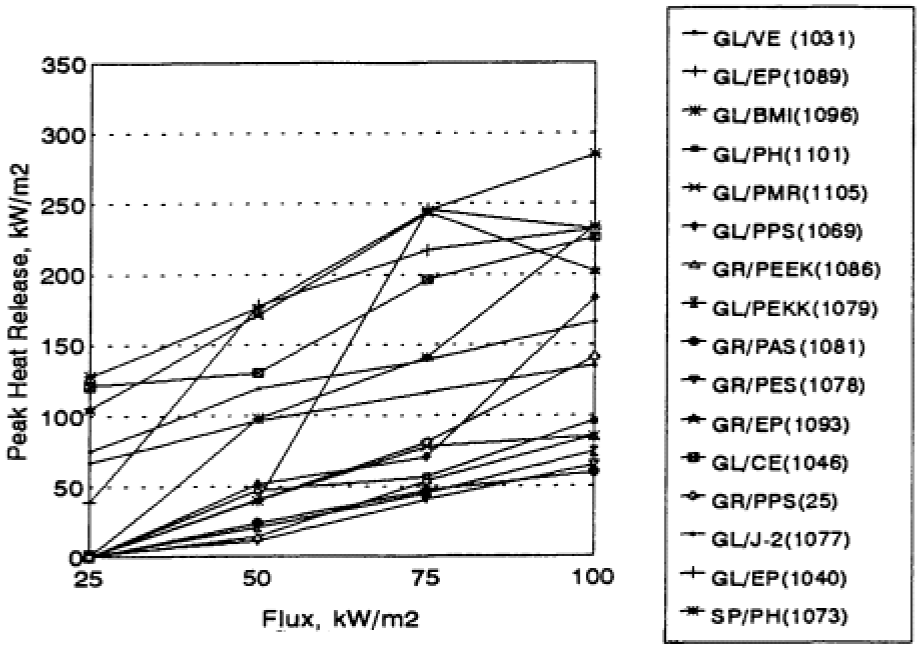

FIGURE 2 Peak heat release versus flux for selected composite materials.

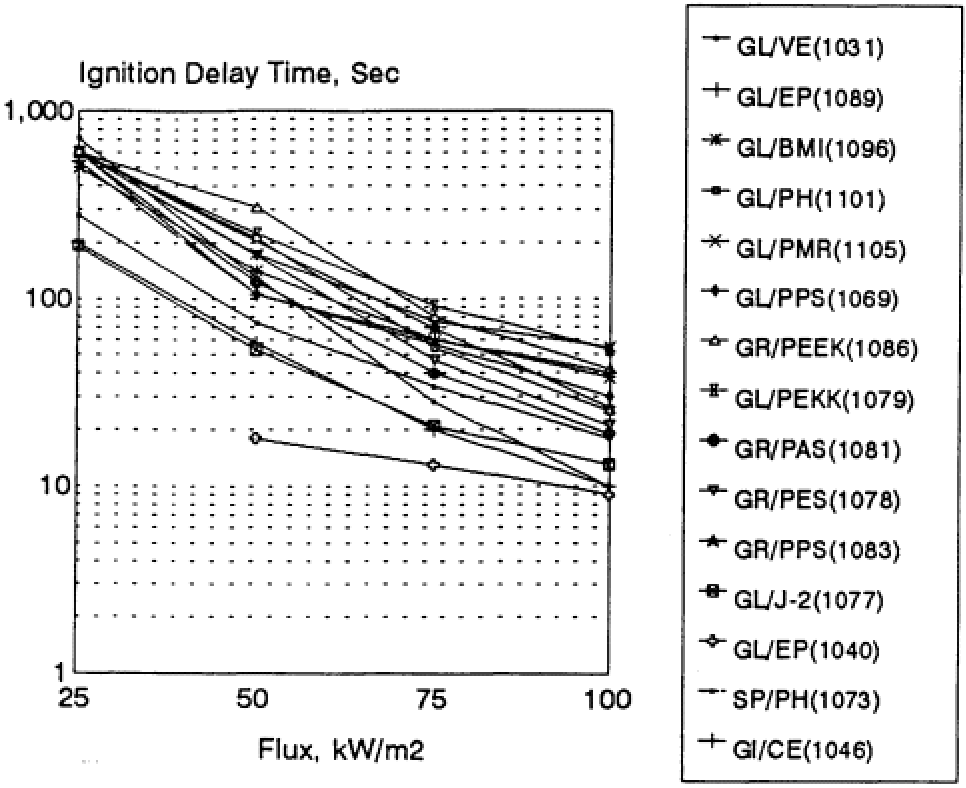

FIGURE 3 Ignitability of composite materials.

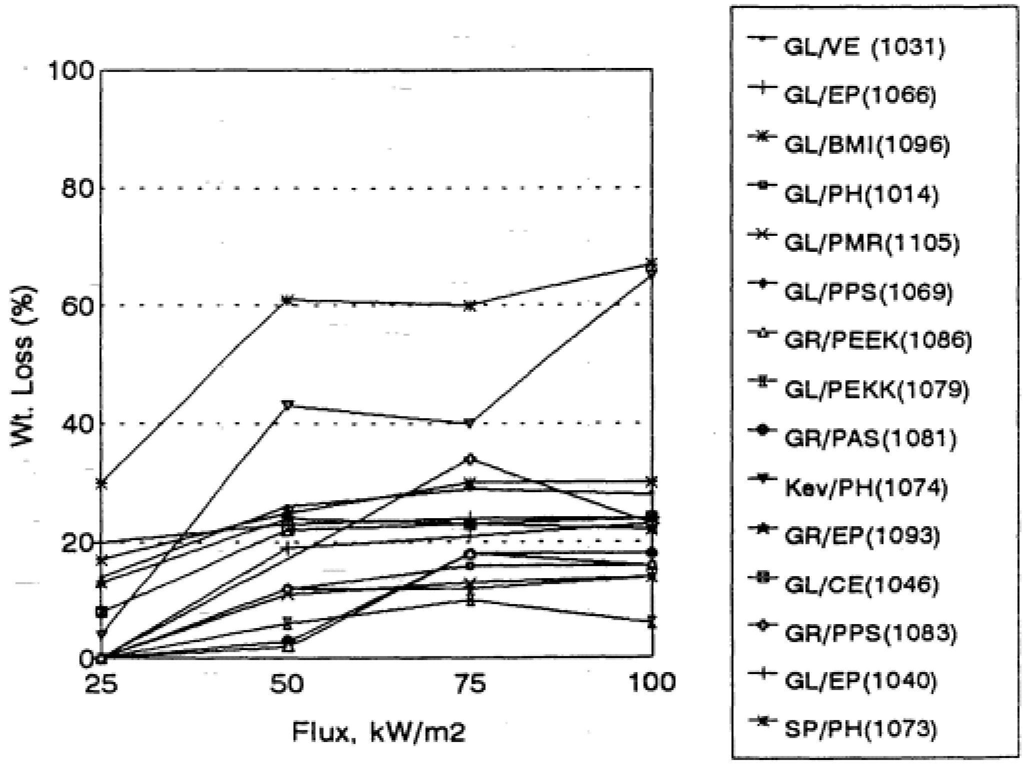

FIGURE 4 Weight loss (%) for selected composites.

TABLE 7 Oxygen Index for Selected Composites

Composite	Oxygen Index
Glass/VE (1031)	34
Graphite/epoxy (1092)	33
Glass/BMI (1096)	65
Graphite/BMI (1097)	55
Graphite/BMI (1098)	60
Glass/PPS (1069)	64
Graphite/PEEK (1086)	58
Graphite/PAS (1081)	66

There are basically two types of matrix resins used in composite industry. These are thermosets and thermoplastics. Thermosets are cross-linked polymer chains in which composites degrade, thermally decompose, or char, but do not melt or drip. Thermoplastics are mostly linear polymeric chains that tend to soften when exposed to higher temperatures. Low-temperature thermoplastics also tend to drip. The fiber most commonly used for naval applications is glass, and graphite fiber is used predominantly for aerospace applications. Special applications such as ballistic armor employ aramid, and radome-related applications may use polyethylene fibers. The extinguishment of fire depends on the fire-propagation rate, physicochemical properties of the materials, and the rate of application and the concentration of extinguishing agents. Water applied through sprinklers is the most widely used liquid extinguishing agent (Macaione and Tewarson, 1990).

Heat Release and Ignitability

The "authors" of MIL-STD-2031 extensively discussed the significance and effects of heat release rates with researchers inside the navy laboratories and also outside the Department of Defense community, and came to a conclusion that materials that exhibit peak and integrated heat releases per unit time below 50-60 kW/m² are considered as "good" materials.

There appears to be a significant difference in the burning mechanisms of thermoplastics and thermoset materials. Thermoplastics (AS-4/PEEK, AS-4/PPS) burn, after ignition, for a longer period of time but produce lower peak heat release rates. The thermoset materials, in general, burn for a shorter period of time and produce much higher heat release rates. If the heat released per unit time during a fire is low, the ability of the fire to spread is limited. Furthermore, a lower heat released per unit time also protects the sailors aboard submarines who must respond to fires quickly and who often use fire extinguishers requiring a close approach to fire.

Ignitability is defined as the ease of ignition. The higher the heat flux, the shorter the time before ignition. In general, time to ignition may also be looked upon as the thermal resistance of the polymeric material to participation in the fire scenario. It is in this area of material development where great strides have been made in the past 10 years due to the need to use higher and higher glass transition temperatures for higher and higher speeds in the aircraft industry.

The ability of a material to resist ignition is an important consideration for ensuring adequate response time and minimizing the spread of the fire. For submarine interior materials, the Navy criteria at thermal insults of 25, 50, 75, and 100 kW/m² are minimum ignition times of 300, 150, and 90, and 60 seconds, respectively. The ignition time criteria were established from "typical" response and fire-fighting times aboard submarines.

Influence of Fiber Reinforcement

The type of fiber reinforcement can also influence the fire performance. Composites with glass fiber or graphite fiber reinforcement smoke less and give less heat output than composites with organic fibers such as ultra high molecular weight polyethylene or aramid fiber due to their combustible nature. Also, heat transfer through the thickness of the composite results in higher temperature gradient for glass-reinforced composites than with graphite-reinforced composites due to differences in thermal conductivity. Thick reinforced composites have also shown a tendency to reflash if not cooled properly when extinguishing the fire.

Effect of Resin Matrix and Additives

Comparison of flammability data for previous thermoset composites shows that phenolic and polyimide composites smoke less, have low flame spread, have high ignition delay (more difficult to initiate), have low peak heat release, have low total heat release, and have a high oxygen index. Also, thermoset composites char during fire exposure due to a high degree of cross-linking. The char formation, highly pronounced in phenolic composites, tends to insulate the core of composite structure and thus render less structural damage.

Comparison of flammability data for various thermoplastics shows that all advanced thermoplastics, in general, have low flame spread, low-smoke density, and low heat release values. However, thermoplastics have low ignition delay times, with PEEK and PEKK being the exception. The repeat unit of PEEK is very similar to that of phenolic resin, which is inherently fire-resistant due to the high cross-linked cure structure. It is assumed that the fire resistance is primarily due to the aromatic character. However, the pendant phenolic (-OH) group may also contribute to the fire performance. The argument about the aromatic character is in agreement with thermoplastics such as PEEK or PPS. Both have benzene linkages with pendant groups in polymer chains. However, phenolics are cured via polycondensation reactions in which water is released. This causes higher void content, and thus phenolic matrix composites are not suitable for primary structures. A number of U.S. corporations have begun some research work in the past few years to alter the cure chemistry of phenolic resins from polycondensation to addition reactions in which no volatiles are released during curing. These include work in phenol triazine (PT) resin technology that is based on the thermally and chemically stable network derived from the cyclotrimerization of cyanate ester groups, and polycondensation of phenol-free phenolic resins with bisoxazolines without producing volatiles during the curing cycle (SAMPE, 1988).

The type of matrix resin used has a significant impact on the toxicity of combustion gas generation and corrosivity of gases on surrounding equipment or instruments. The most common of toxic gases evolved during combustion is carbon monoxide. In addition to carbon monoxide, fluorocarbons will produce hydrogen fluoride (HF), chlorinated resins will produce HCl, sulfur containing materials will produce hydrogen sulfide (H_2S), and nitrogen-containing materials will produce HCN. The nature of the combustion mechanism during fire exposure may also have a significant impact on the toxicity of combustion gas generation; this is the case with phenolic composites, which tend to char and smolder, giving off higher amounts of carbon monoxide due to incomplete combustion.

Modification of resin matrix can also have a significant impact on fire performance of composites. This modification can be in the form of additives, such as rubber for toughening the epoxy-based composites, fire retardants for vinyl esters, or chemical reformulation such as replacing aliphatic diamine with aromatic diamine. Addition of antimony trioxide and hydrated alumina to the polyester and epoxy resin systems significantly decreases (improves) flammability characteristics but causes a marked increase in smoke evolution. Additives also cause reduction in load-bearing characteristics of composite structures. Chemical modification offers a viable alternative to improving flammability characteristics. Chemical modification of polyimide increased the ignition delay times from 75 to 123 seconds and from 55 to 68 seconds, respectively, when exposed to radiant heat fluxes of 75 and 100 kW/m^2 during Cone Calorimeter heat release testing.

Resin content of composites can also have a significant impact on composite fire performance. In general, the higher the resin content, the higher the smoke and heat release. Various fabrication techniques can influence the fire performance of composites. Autoclave composites have, in general, a higher volume fraction of fiber and better fire performance; also, thermally cured composites, in general, have better fire performance than room temperature cured composites due to higher degree of cross-linking.

Residual Strength

Advanced composite designs take advantage of different ply orientations to maximize load-bearing characteristics. For epoxy-based composites, this results in poor residual flexural strength due to resin charring and subsequent loss of interlaminar strength between plies. Woven roving as the structural reinforcement provides higher residual flexural strength during fire exposure for marine structures. As noted earlier, since thermoplastics soften during heating, measurements of flexural strength retained after fire testing may not give true or accurate flexural properties during fire. The potential for increased use of organic matrix composite structures will not be realized until the measurement, analytical prediction, and validation techniques for structural integrity during and after fire exposure have been established.

ACKNOWLEDGMENTS

The authors wish to acknowledge the contributions of many people at CDNSWC for their technical assistance. These include James Morris, Charles Rollhauser, Michael McFarland, Thomas Gracik, Timothy Dapp, Thomas Nixon, and Dr. Gene Camponeschi. The authors also wish to thank and acknowledge the constant support and encouragement of Dr. Eugene Fischer, Ivan Caplan, and Terry Morton.

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Fire Properties of Future Material Candidates

Charles A. Wilkie[*]

BACKGROUND

If we wish to look at future materials that may provide a safer fire environment, it is useful to first consider the past. Currently we attempt to produce fire-safe materials by the additive route and by the synthesis of materials that one hopes may be inherently more fire safe. The additive route means that something is added to the polymer, either in a physical or a chemical fashion, to make that material more resistant to burning. The commonly useful additives include alumina trihydrate and magnesium hydroxide, halogens, phosphorus, antimony, and synergistic combinations of these, sometimes including nitrogen or other elements.

Additives may function in the vapor phase, as radical scavengers to quench the flame, or in the condensed phase. Condensed-phase retardants either change the mode of degradation of the polymer so that the production of volatile species is reduced or promote the formation of a thermally insulating char layer on the surface of the polymer; frequently the mode of degradation is changed to one that produces char. This char layer insulates the feedback of energy from the fire to the polymer and tends to prevent volatilization of material from the polymer. Condensed-phase retardants offer, in my opinion, the best chance to retard the burning of polymers because they provide a means to prevent, rather than quench, a fire. Currently, vapor-phase additives are more commonly used, but I believe that this will change in the future.

Alumina trihydrate (ATH) and magnesium hydroxide decompose endothermically and remove heat so that all of the applied heat is not directed at the polymer. They also release water, and some of the energy is taken on by the water. These additives are effective, but very large loadings are required, and this has a deleterious effect on the physical properties of the polymer.

Halogens, mainly bromine compounds but to some extent also chlorine compounds, form HX in the vapor phase. This will interact with the hydrogen and hydroxy radicals that make up the flame and remove them so that the flame is quenched. Again, these materials are effective but present a problem because a great amount of HX is released. Many compounds of phosphorus, including elemental phosphorus and phosphates, have been used and are currently being used as flame-retardants.

The majority of additives that have been used as flame-retardants for polymers in the past have relied on action in the gas phase. These materials do quench fires, but they offer disadvantages due to toxicity and loading.

A very significant problem is the lack of portability of additives from one polymer to another. Because most flame-retardants have been devised based upon a trial-and-error approach, there is little knowledge about how the additive interacts with the polymer. This means that no

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one can predict if an additive that is effective for one polymer will be effective for another polymer.

A PREDICTION OF THE FUTURE OF FLAME RETARDANCY

The route to the future is clear. Both the synthesis of new polymers that incorporate flame-retardant elements and the use of condensed-phase additives will continue. We must continue to perfect the additives and the kind of chemistry that these additives perform and we must develop new additives that will perform new chemistry. The role of heat release rate in the evaluation of a potential flame-retardant system must be considered.

It is my contention in this paper that the continued use of the trial-and-error method of additive selection that has been followed for years will not prove especially fruitful. The role of flame-retardant elements is, for the most part, well known; some of the modes of action are delineated above. As in almost any somewhat-mature area, only incremental improvements are to be expected if one follows the path well trodden. Major advances (and major disappointments) may occur from new approaches.

In this paper I suggest new routes that may be explored in order to develop the flame-retardant systems of the future. In essence, I suggest that we must forget about the so-called flame-retardant elements and, instead, concentrate on chemical reactions that will change the degradation pathway of the polymer so that a cross-linked char is produced on the surface of the polymer rather than a significant fraction of volatiles.

Most thermoplastics degrade to produce little, if any, char and high yields of volatiles. Some of the newer, high-performance engineering thermoplastics, such as polysulfones or polyetherketones, give high char yields with low heat release rates. One model for the future is to produce thermoplastic systems that will char in the same way as these engineering thermoplastics. Continued development in the high-performance engineering thermoplastics to make them even more thermally resistant is also required.

Char formation to give an adherent, thermally insulating layer on the surface of the polymer prevents the feedback of thermal energy to the underlying polymer and effectively prevents its burning. Char formation offers the opportunity of portability from one polymer to another, and this offers great possibilities for the design of new flame-retardants. I believe that we must begin to design flame-retardants to perform a specific task upon interaction with the polymer and that a systematic investigation of reactions between polymers and additives will enable this design. A schematic diagram showing how char formation may proceed and its effect is shown in Figure 1.

In this diagram, at the top, a thermoplastic is shown. If one adds energy, that is, increases the temperature, bonds may begin to break. Bond cleavage will give rise to small molecules that can escape from the polymer and enter the flame zone. If one finds the reagents that are necessary to cross-link the polymer strands, then, when the same amount of thermal energy is added to the polymer, bonds will still break; however, the strands will still be attached to the polymer and no volatiles can escape. Significantly greater temperatures are required to break the bond that will liberate the small molecules and give rise to a flame. Recent work from the National Institute of Standards and Technology (NIST) has provided theoretical support for the concept of cross-linking to provide flame retardancy (Nyden et al., 1992).

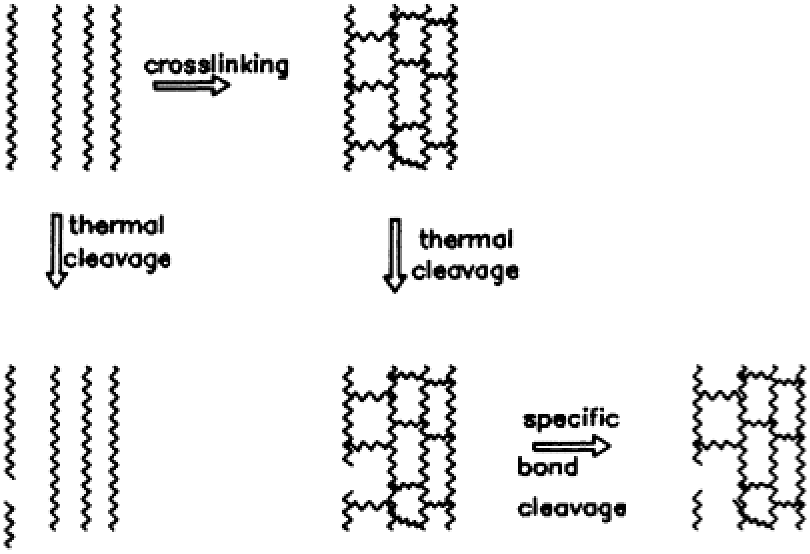


FIGURE 1 Schematic representation of the formation and effect of char.

It must be considered that an organic polymer will always eventually burn. We can attempt to increase the ignition temperature and to reduce the evolution of toxic gases and smoke from the material, but it will eventually burn. If we wish to have materials that will not burn, then we are forced to consider inorganic materials. Phospham is an iminophosphazene polymer of unusually high thermal stability, and this material, either by itself or in combination with other polymers, offers some potential (Weil and Patel, 1994). Other inorganic polymers also offer promise, but this topic, as well as the synthesis of new inherently flame-retarded polymers, is outside the scope of this paper. This paper is limited strictly to an examination of some of the types of reactions that might be performed on polymers with the goal of char formation. Some of these reactions will be limited to specific polymers, others will be more broadly applicable.

A problem currently facing the designer of flame-retardants is the lack of applicability of an additive from one polymer to another. This is a most unfortunate situation. It is imperative that we have a detailed understanding of the interaction of an additive with a polymer so that one may predict the applicability of an additive to another polymer. Our goal should be to develop somewhat complete mechanistic information about the course of the chemical reactions that ensue between the polymer and the additive; only in this way can one learn if a particular additive will be useful with another polymer.

Temperature Requirements

For any flame-retardant reaction that one may consider, it is important to allow no reaction under normal conditions of temperature. The normal temperatures to which a polymer is exposed go up to the processing temperature of that polymer. Thus, there must be no reaction until the temperature is above the processing temperature with some margin of safety. A realistic measure of the margin of safety is about 50 °C; practically, this means that the temperature at which the reactions to be considered commence must be at least 300 °C. The higher the temperature, the greater the possibility for degradation reactions of the polymer, so the onset temperature for the reaction must not be unduly high. It is probably useful to consider an onset temperature of 300 °C to 350 °*C.*

Types of Reactions

For the purposes of this paper, I have arbitrarily divided reactions into three classifications: oxidation-reduction reactions; acid-base reactions; and organic reactions. This is a very arbitrary distinction, but it is a useful way to keep track of reaction types.

Oxidation-Reduction Reactions

The ultimate products that are obtained when an organic polymer is burned are carbon dioxide and water. The possible oxidation states that are available to carbon range from -4 to +4; of course, in carbon dioxide, the oxidation state of +4 is attained. In a typical polymer, the oxidation state of carbon will range between slightly negative numbers to values near zero. This means that one can carry out an oxidation to increase the oxidation level by only a little, perhaps up to the level of zero, which describes graphite. There is a wide variety of reagents that are regularly used in either inorganic or analytical chemistry as oxidants, including permanganate, dichromate, nitrate, elemental chlorine or bromine, and others. In addition, there are many much-milder oxidizing agents that may prove useful. These include both the transition elements, which have two possible oxidation states (e.g., iron), and those nontransition elements that have more than one accessible oxidation state (e.g., tin).

Oxidation may be most useful for those polymers for which the average oxidation state of carbon is relatively low. This may mean that oxidation would be most applicable to hydrocarbon polymers and not those that contain functional groups. Since very little, if any, of this chemistry has been performed, it is difficult to make general statements. The choice of oxidizing agents is not an easy one, especially considering the severe temperature requirements. A strong oxidizing agent will likely effect reaction at lower temperatures so the probable initial choice is a somewhat weak agent whose strength may increase with temperature. The Nernst equation tells us that, in aqueous solution, the potential for any reaction will increase with temperature. Oxidation reactions will not be performed in aqueous solution, but it is reasonable to assume that the oxidation potential will increase with temperature. Thus, oxidizing agents such as Sn^{4+} and Cu^{2+} may be a good starting point. The exact choice of materials to be studied is probably somewhat unimportant. The idea is to determine if the use of oxidizing agents is a valid approach to flame retardancy. Thus, nitrate, and even permanganate, should be examined. At the recent American Chemical Society meeting, Zaikov's presentation focused on oxidizing agents (Zaikov, 1994). The message that he imparted to the audience was that "oxidation is your friend." These preliminary results are all that is available, but they do suggest that this may be a fruitful area for investigation.

The expectation is that an effective oxidizing additive will increase the char yield in a thermogravimetric analysis. The first step in this area would be to compare various classes of polymers with a selection of oxidants and determine by thermogravimetric analysis (TGA) the weight-loss behavior. Note that even though it is expected that oxidizing conditions will be most effective for hydrocarbon-type polymers, it is not recommended that only these be examined. It is important to have a comparison between polymer types to understand how and why the reactions occur and learn how to apply them. Even better than this would be to perform a TGA-Fourier Transform Infrared (FTIR) experiment and compare the starting polymer with the polymer-additive combination. The advantage of this approach is that it permits not only the determination of the fraction of weight that is lost but also an identification of the gases that give rise to that weight loss (Mittleman et al., 1994). It is also important to perform cone calorimetry to determine the rate of heat release and associated information.

If oxidation is useful for polymers in which the average oxidation state is fairly low, then reduction may be most useful for those polymers in which the oxidation state is fairly high, such as functionalized polymers, especially those that contain carbonyls. The collection of reducing agents is not as large as that of oxidizing agents. In an inorganic or analytical laboratory the common reducing agents are metals, especially the alkali metals. These clearly cannot be used for polymers, and some other material must be sought. In principle any metal can behave as a reductant; thus, the incorporation of metals into polymers may effect reduction. Metals that should be considered include zinc, manganese, aluminum, iron, and chromium. These metals include the strongest reducing agents that have reasonable water stability. One of the more potent, yet usable, inorganic reducing agents is Cr^{2+}. The chemistry of chromium (II) is controlled by the fact that compounds containing this ion exist as multiple metal-metal bond species (Cotton, 1978). The ligands surrounding the metals control the bond length and probably the reactivity. This species may easily be oxidized to the Cr^{3+} state. The oxidation of Cr^{2+} is so facile that in some compounds air is able to effect the oxidation. The choice of ligands that surround the low-valent chromium dictates its ease of oxidation and, thus, its ability as a reducing agent.

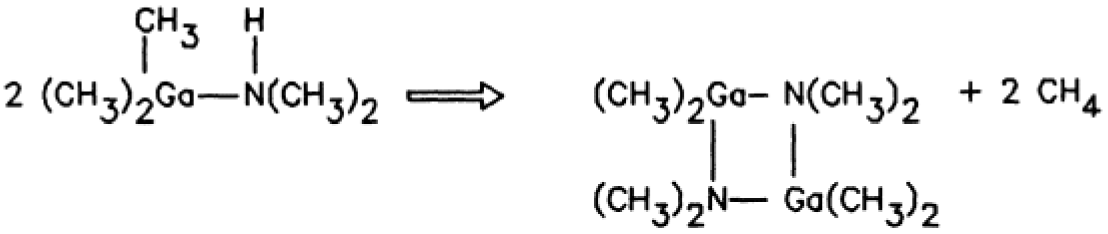
The logical starting point for the investigation of reducing agents is to blend Cr^{2+} in one of its many forms with a variety of polymers that contain carbonyl groups or similar functionalities which will lead to a relatively high oxidation, as well as with some hydrocarbon polymers, to check on the question of the importance of oxidation number. It must be recognized that Cr^{2+} is a somewhat exotic reducing agent. I am not proposing this as a flame-retardant but rather as a starting point to learn about the effect of reducing agents on the thermal degradation of polymers. In addition, these same polymers should be combined with some of the metals mentioned above to determine the relative effectiveness of the two different classes of reductants.

Another oxidation-reduction reaction is oxidative insertion into some bond. This reaction may not be immediately recognized as an oxidation. The normal material that will participate in an oxidative insertion is some transition metal compound that does not fulfill the 18-electron rule. An example of this is Wilkinson's catalyst, $ClRh(PPh_3)_3$, which is best known as a homogenous hydrogenation catalyst. In work that has been performed in my laboratories at Marquette University, we have shown that this material will insert into a C-O bond of compound is such that it could never be used as a flame-retardant, but it is important to examine the potential of such reactions and to use them to identify other materials that may be useful. Since this rhodium compound functions as a hydrogenation catalyst, other hydrogenation catalysts should be investigated, not only with PMMA but also with other polymers, to determine the breadth of this reaction (Collman, 1968).

Acid-Base Chemistry

There are two different types of acids and bases, Bronsted and Lewis. A Bronsted acid is defined in terms of its ability to donate a proton while a base is a proton acceptor. Thus, Bronsted chemistry will only be important in those cases where the polymer contains acidic or basic functionalities. This severely limits our ability to affect a polymer based upon this chemistry. For those special cases where the polymer is acidic, for example, poly (methacrylic acid), the presence of some basic additive that will react only at elevated temperatures may cause cross-linking through ionomer formation. Again there is the problem of temperature and acid-base strength. For a polymer like poly(methacrylic acid), the basic additive must be one that will not react at room temperature but will react at elevated temperatures. This means it must be a very weak base at room temperature, and, because cross-linking is the goal, it must be difunctional. I am not convinced that this area can lead to much useful chemistry.

The Lewis description of acids and bases is more useful for our consideration. A Lewis acid is defined as an electron pair acceptor, and a Lewis base is an electron pair donor. Any polymer that contains either oxygen or nitrogen will have Lewis basicity, and it may be possible to react this with a Lewis base. The reaction of choice would utilize a bifunctional Lewis base so that it can bridge two groups and effect cross-linking. Unfortunately the dative bond between the acid and base is not very strong and will probably be cleaved easily at reaction temperature. It is possible to design the Lewis base such that it may undergo further reaction with the polymer so that the bond is converted into a strong covalent bond. An example from organometallic chemistry is shown in Figure 2.



$$2\ (CH_3)_2\overset{\overset{\displaystyle CH_3}{|}}{Ga}-\overset{\overset{\displaystyle H}{|}}{N}(CH_3)_2 \Longrightarrow \begin{array}{c} (CH_3)_2Ga-N(CH_3)_2 \\ |\qquad\quad| \\ (CH_3)_2N-Ga(CH_3)_2 \end{array} + 2\ CH_4$$

FIGURE 2 Example of organometallic chemistry.

In order to carry out this chemistry it is necessary that there be a group on the polymer that may thermally combine with some group on the Lewis base. This will require very careful design but does offer some potential for polymers. As an example of this chemistry, I cite the work of McNeill on blends of zinc bromide and poly(methyl methacrylate) (McNeill and McGuiness, 1984a, b). The Zn^{2+} ion acts as a Lewis acid, coordinating to the carbonyl oxygens. A thermal reaction then leads to the evolution of methyl bromide with the formation of a zinc salt of poly(methacrylic acid).

It is obvious that this type of chemistry will only be effective for those polymers that contain Lewis basic sites; there should be no effect on hydrocarbon polymers. The logical starting point is to carry out reactions involving various Lewis acids—zinc and tin compounds come immediately to mind—to see what the effect of these will be on the degradation of the polymer. In my laboratory, we have investigated reactions of PMMA with several different tin compounds that may have some acidic character at elevated temperatures (Chandrasiri and Wilkie, 1994a, b). The results of these investigations indicate an increase in char formation with the formation of tin salts of the polymer. The ligands on the tin give volatile materials that can easily burn. It will be necessary to carefully design the additive that is used so that the fragments that are lost from the acid will not contribute to the flammability of the polymer-additive blend. This may be accomplished by using a reactive rather than an additive and actually having the Lewis acid be a part of the polymer backbone. These investigations must be extended to other polymers in order to explore the generality of these reaction systems.

Organic Reactions

There is a wide variety of organic reactions that may be considered. These may be classified as addition, substitution, and elimination reactions. An addition reaction means that something is added to the substrate, usually addition across a multiple bond. In the majority of polymers, double bonds are absent, so addition reactions may prove useful only in limited cases. These limited cases include polybutadiene, copolymers containing butadiene, and related materials. Here it may be possible to perform some addition reaction across the double bond. The ideal material to add is some difunctional compound that can effect cross-linking of the polymer. The first possibility that comes to mind is some α, ω species that can form a diradical under thermal conditions and may add across the double bonds in two different polymer strands and effect cross-linking.

The Diels-Alder reaction may also be utilized for materials that contain double bonds. The polymer strands can function as the dienophile and some additive as the diene. The normal reactive dienophile contains functional groups that activate it for this reaction. In this case, since we do not want reaction to commence until elevated temperatures are reached, it may be an advantage that the polymer is not activated. The diene must be chosen carefully so that it will be thermally stable, yet not volatile, at flame temperatures. The choice of diene will be critical to the success of the reaction.

There appears to be no work performed on Diels-Alder chemistry on polymers; this is not surprising because the double bond in a butadiene unit is an unactivated, and, therefore, an attractive dienophile. Thermal activation is a distinct possibility, and it is recommended that attempts be made to model this reaction with simple dienes to determine if the reaction has potential for achieving cross-linking of polymers.

Substitution reactions should prove more useful than addition reactions. In a substitution reaction, one replaces one atom or group with another. Friedel-Crafts substitution reactions may prove useful for aromatic systems (Brauman, 1979; Rabek and Lucki, 1988). If one can identify a suitable catalyst that will function only at high temperatures, then a difunctional additive can easily be identified to effect this reaction. The usual catalysts for Friedel-Crafts chemistry are strong Lewis and Bronsted acids. Strong Lewis acids are not suitable because they are hydrolytically unstable. A Bronsted acid, on the other hand, should increase in strength as temperature increases. This implies that a Bronsted acid, which is weak at room temperature, may become strong enough at elevated temperatures to function as an effective catalyst for the reaction. The alkylating or acylating reagent that is used must be at least difunctional; the usual reagent is a halide. A halide would be unsuitable here because it would lead to the evolution of HCl. Alcohols have also been used as alkylating agents for Friedel-Crafts chemistry, and these offer the great advantage that water is the byproduct. Not only does this remove the toxicity problem, but the presence of water will dilute the flame, and some heat will be wasted in heating up the water rather than the polymer. This type of chemistry appears to offer a real advantage for polymers that contain aromatic rings, such as polystyrene and copolymers containing styrene.

The problems then that are presented in making Friedel-Crafts chemistry a viable means for cross-linking of benzene rings in styrenic and related polymers are two: catalyst and alkylating/acylating agent identification. The catalyst must be completely ineffective at modest temperatures but become effective when the polymer is subjected to a thermal stress. The catalyst must "turn on" at about 300 °C and promote the reaction. The akylating or acylating agents must be difunctional, nonvolatile at fire temperatures, and thermally stable. The best alkylating agents will probably be based upon aromatic chemistry so that the stronger aromatic bonds will be available for thermal resistance.

Substitution reactions for nonaromatic substrates will no doubt involve the functional groups on the polymer in some way, and these reactions will be dealt with later. Elimination reactions invoke the loss of some species with the formation of a multiple bond. This reaction is well known in polymer degradation because it is the pathway by which polymers, such as polyvinylchloride (PVC) or polyvinyl acetate, degrade. In this arena, this reaction is known as chain-stripping. The degradation of PVC is shown in Figure 3. One way in which this reaction may prove useful would be in combination with an addition reaction. If a polymer, such as PVC could be activated to undergo chain-stripping and if there were an additive present that could add to that double bond and effect cross-linking, this would be a desirable result. This is rather exotic chemistry because a minimum of two additives are required: one to facilitate the chain-stripping reaction and one for the addition. This is not likely to be an area where immediate progress can be made.

Functional Group Reactions

The great majority of polymers contain functional groups. These functional groups include esters, acids, nitriles, ketones, and halides. The literature of organic chemistry is replete with examples of reactions that may be carried out on these various functional groups. In small-molecule chemistry these reactions are normally designed to convert one material into another.

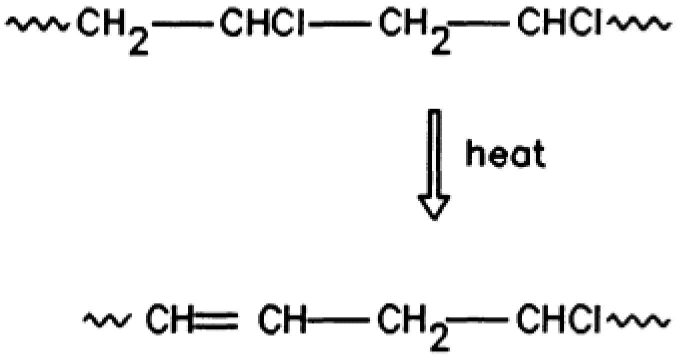


FIGURE 3 Degradation of polyvinylchloride.

In this arena, we would be looking for processes that could effect the cross-linking of the polymers. This is a straightforward extension of the types of organic reactions that have been carried out for many years, and a collaborative effort between one who is versed in flame retardancy and one who is versed in organic reactions should lead to some interesting results.

As an example of this type of chemistry, I will cite the fact that a hydrogen that is adjacent to a carbonyl group is more acidic than other hydrogens. Use may be made of this to effect an alkylation at a site adjacent to the carbonyl. If one uses some difunctional alkylating agent, it is possible to effect cross-linking of the polymer chains.

Systematic Studies of Additives and Polymers

I think that it is important that one think not only about materials that may be used as flame-retardants but also broadly consider various classes of compounds and reaction types. If we can learn how a particular class of reagents interacts with a variety of polymers, we can then use this information to begin to design an additive (or reactive) flame-retardant that will participate in the desired reaction. In this regard I mention the great number of investigations that have been carried out in McNeill's laboratory and in my laboratory on the effect of additives on the thermal degradation of PMMA (Camino et al., 1978; Jamieson and McNeill, 1978; Wilkie et al., 1981, 1991a, b; McNeill and McGuiness, 1984a, b; Brown et al., 1986; McNeill and Liggat, 1990, 1992; Beer et al., 1992; Chandrasiri et al., 1994; Chandrasiri and Wilkie, 1994a, b). The combined knowledge that results from the sum of these investigations should be enough to lead one to begin the process of designing additives that will be useful for flame retardance of PMMA. It is only when we understand how an additive affects the chemistry of degradation that we can apply that additive to other polymers. It is imperative that systematic, mechanistic studies on the effects of additives on the thermal degradation of polymers begin soon.

Surface Treatment of Polymers

Of all of the current schemes used to achieve flame retardancy, I believe that only one, intumescence, will stand the test of time and continue to be used into the next century. Intumescent flame-retardant systems are those that thermally form a voluminous foamed char layer that protects the underlying polymer (Camino et al., 1978, 1984a, b, c, d, 1985a, b, 1988, 1989, 1990a, b, 1991; Camino and Costa, 1986, 1988; Impallomeni et al., 1986; Bertelli et al., 1989a, b, c; Marchal et al., 1994). An intumescent system consists of an inorganic acid or a compound that thermally generates an acid and a polyhydric compound in addition to the polymer to be protected. Ammonium polyphosphate and pentaerythritol have been used with a polymer such as polypropylene. In the condensed phase these will form a multicellular char layer on the surface of the polymer. The intumescence approach has great appeal because it appears to offer applicability to a variety of polymeric systems.

The mechanism of intumescence is now somewhat understood for the ammonium polyphosphate-pentaerythritol-polypropylene system. There has not been much application to other polymeric systems, and this approach must be extended to other polymers. It is also necessary to determine the best choices for the acid former and the char former. The question of potential toxicity of these additives must also be addressed.

An alternative process to form this char layer is to graft some char-forming monomer onto the polymer. If one is able to graft a monomer onto the surface of the polymer that will thermally decompose before the polymer does, then this can form an adherent char layer on the surface that will effectively insulate the polymer from the flame and prevent degradation. In my laboratory we have had success using methacrylic acid grafted onto acrylonitrile-butadiene-styrene terpolymer, ABS. When the methacrylic acid is converted to its sodium salt by treatment with sodium hydroxide, this offers extensive protection to the underlying ABS (Suzuki and Wilkie, 1995). Of course, it may not be necessary that the char-forming layer be chemically attached to the polymer. It may be sufficient that there merely be a layer of char former at the surface of the polymer. The importance of chemical attachment versus physical attachment of this layer to the polymer remains to be seen.

One of the significant advantages of this approach is that it should be applicable to a wide variety of polymers. If one can apply a surface layer of poly(sodium methacrylate) or some other good char former to a polymeric substrate, either by physical or chemical means, and if this degrades to char before or at the same time as the substrate degrades, one has an effective flame-retardant system. Further developments in this area require the identification of suitable char formers whose degradation temperatures are known, along with suitable methods to apply this to the appropriate substrate. A variety of char formers is required because one will need to "tune" the degradation temperature of the char former to that of the substrate. These systems must be optimized to determine the match that is required between degradation temperatures of substrate and coating.

Experimental Protocol

Many reactions have been suggested in this paper, and evaluation and determination of how to spend limited resources to maximize the return have a critical role. I believe that modeling studies on small molecules have a place in this study. Modeling studies are not the first step, however. One must first demonstrate that the indicated reaction will work on the polymeric substrates. For instance, for the redox reactions, the first step should be to carry out a reaction, probably by thermogravimetric analysis, between a blend of the oxidizing agent and several polymers. If an increased char yield for the polymer is obtained, this result would then permit model compound studies. The model must accurately represent the structural features of the polymer and it must be sufficiently nonvolatile to be available at the temperature of the reaction. There will certainly be differences in behavior between the model and the polymer. The model study should be used only to establish some of the steps in the reaction pathway. The actual course of the reaction between the polymer and the additive can then be investigated by the use of TGA-FTIR and related techniques.

CONCLUSION

The premise of this paper is that char formation is desirable to achieve flame retardancy of polymers and that processes that are well understood chemically, and, therefore, extendable to other polymers, are desirable. Reactions that effect the formation of char and have wide applicability to a variety of polymers will be most advantageous. I have presented many different chemical reactions that may lead to the formation of char. It is my hope that the flame-retardant community will have the opportunity to try out many of these reactions and that some may prove to be fruitful.

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Meeting FR Goals Using Polymer Additive Systems

*Edward D. Weil**

INTRODUCTION

Based on experience and theory, it should be possible to find effective low-level additives to further reduce ignitability; heat release rate; and smoke of even the best flame-retardant low-smoke plastics, composites, adhesives, and fabrics. In some cases, there are empirical guidelines; in other cases theory points out promising directions. Even where mechanistic knowledge is sparse, reasonable working hypotheses can point the way to effective additives and, if pursued, also help firm up scientific understanding. The key material properties suggested in mathematical fire models can also provide ideas for additives.

The use of additives should not be viewed as competing with synthesis of new polymeric materials but as a way of complementing, enhancing, and, in the best cases, synergizing the flame-retardant performance of advanced polymers.

TRENDS ON FLAME-RETARDANT COMPOUNDING: BUILDING A SYSTEM OF INTERACTIVE INGREDIENTS

As shown by research in academic laboratories, and by industrial research as disclosed in the recent patent literature, there is a trend toward more multicomponent flame-retardant systems. A system can be built up using a "tool kit" comprising ignition retarders, melt-rheology control agents, mass-transfer retardants, heat-transfer retardants, heat sinks, char initiators, charring catalysts, char-strengthening agents, char-oxidation preventatives, and noncarbon barrier-forming agents. Just as modern rubber and vinyl formulations typically have a substantial number of cooperating ingredients, in the same way we can expect that the most advanced flame-retardant systems will have several additives with, in many cases, positive interactions between them.

In the final optimization stage, computerized statistical methods are available to fine-tune such multicomponent systems, either by traditional experimental design and optimization algorithms (Cornell, 1990) or by more recently developed "neural network" methodology (Gill and Shutt, 1992).

SOME PERSPECTIVE ON THE PROBLEM

Most of the scientific and patent literature in the flame retardancy field relates to enabling flammable commodity polymers to pass fairly lenient small-scale tests such as UL-94. Most of

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the commodity thermoplastics form little char and much volatile fuel. On the other hand, the high-performance engineering thermoplastics, exemplified by polysulfones, polyetherimides, and polyetherketones, have a high char yield and inherently low heat release. There is much less background on making these excellent fire-resistant polymers even more flame-retardant, because the motivation has not been very great. Programs such as that which the Federal Aviation Administration is developing will "push the limits" in new and relatively unexplored territory.

The general strategy for making already good high-char-yielding polymers perform even better with respect to aircraft cabin escape time is to increase their time of ignition, to delay as well as lower the peak rate of heat release, and to retard as well as lower the smoke release. All of these improvements take into account the goal of increased escape time.

SPECIFIC TACTICS

Retardation of Ignition by Reflecting Radiant Heat

In various mathematical models for the rate of generation of ignitable gases, re-radiated heat is subtracted from the externally applied heat (DiBlasi et al., 1991). It follows from other models that increasing the re-radiated heat should retard ignition (Dimitriou et al., 1989; Delichatsios et al., 1991).

Empirical work done in Russia on this aspect with decorative plastics showed that spectral reflecting capacity of the materials was important in controlling the ignition time under radiant heating conditions (Shabalin and Mozolevskaya, 1989). Factory Mutual work has also shown a large difference in ignition time between dark-coated and uncoated polymethylmetacrylate (PMMA) (Tewarson, 1994). Absorptance of radiant heat by different varieties of wood, in relationship to the spectral distribution of the ignition source, has been shown to have a major effect on the time of piloted ignition of wood (Wesson et al., 1971).

The opportunity to retard ignition by using a reflective surface seems perhaps to have been overlooked in plastics flame-retardant technology, although protective clothing and fire fighters' gear with heat reflective properties have been successful in the field.

On the empirical side, it is common knowledge that light colors reflect heat better than dark colors, and the choice of color for clothing, vehicles, and houses often makes use of this factor. It is probably less commonly a matter of experience that the effect can be dramatic with very high irradiances. Photographs taken after an atomic bomb blast show this. In one instance, the pattern of a kimono was thermally etched onto the back of a Hiroshima survivor. In another instance, a shirt exposed to the same heat source shows the dark stripes carbonized whereas the white stripes are not even scorched.

Designers of commercial aircraft cabin interiors usually incline toward light shades but the colors are decided on aesthetic considerations. The spectral behavior that matters the most is not visible light absorption but infrared. Perhaps this factor should be taken into account or put on a sound scientific basis, or even made the subject of regulation.

Looking again at ignition theory, we find a number of models, ranging from theoretically derived to empirical. Without presuming to get into a discussion of their merits, we can note the input variables that occur in these ignition models. Empirical studies show that ignition is more complicated than it seems at first examination. The evolution of a fuel which in admixture with air gives an ignitable composition is a first requisite; but, in the absence of a pilot flame, a combination of conduction and infrared absorption by both the vapor and the surface is decisive (DiBlasi et al., 1991). Catalytic wall effects can influence ignition either positively or negatively (Vlachos et al., 1994).

It has been known for a long time that piloted ignition time is a function of incident irradiation, the spectral distribution of the ignition source, and the optical properties of the material (absorptance and re-radiation).

A mathematical model derived at the University of Oklahoma (Hallman et al., 1972, 1974) involving terms for reflectivity and absorptivity provides a surprisingly good correlation to observed ignition time, considering that the data are taken from the literature and also that one of the terms in the equation is surface ignition temperature, the measurement of which is fraught with difficulties. Some appreciation of these difficulties can be gained by noting the exchange of views between two groups of researchers trying to measure the same ignition temperatures (Thomson and Drysdale, 1987; Drysdale and Thomson, 1988; Kashiwagi, 1988).

It is quite possible that reflective pigments such as titanium dioxide (TiO_2) or, even better, the pearlescent pigments comprising TiO_2 deposited on mica, and various infrared reflective clays, may be useful and practical for ignition retardation. This topic has been scarcely studied. Obviously, the reflective pigments would be rapidly defeated by surface charring.

Raising Ignition Temperature and Effective Heat Capacity by Providing Heat Sinks

There is scattered evidence that the heat sink effect is an important mode of action for additives such as melamine in lower-temperature polymers such as urethane foams (Batt and Appleyard, 1989). The heat capacity effects alone were used to explain the relative effectiveness of halogen compounds in the flame (Larsen, 1974, 1975).

We obtain essentially the same flame-retardant efficacy in an ABS (acrylonitrilebutadiene-styrene) char-former blend from the very stable and nonreactive triphenylphosphine oxide as from triphenyl phosphate, and that suggests that both the phosphine oxide and the phosphate may be at least in part working as a heat sink. This heat sink approach could be extended to high-performance polymers by rational selection of additives, as well as by providing means for the polymer itself to decompose endothermically in the ignition flame spread temperature range.

The heat sink approach need not be inefficient if used in a sophisticated way with a good match of the temperature of the endotherm of the additive to the initial polymer decomposition temperature. One believable German patent reference actually gives data showing an improvement from UL-94 V1 to V0 resulting from the addition of melamine at 1 percent in a complex flame-retarded styrenic system (Feldmann et al., 1989).

In our laboratory at Polytechnic University, we have repeatedly obtained useful incremental flame-retardant effects (V1 improvement to V0) in styrenics and polyamides from addition of melamine in the 5 percent range, likewise with 5 percent triphenylphosphine oxide, in styrenics or polyamides, generally along with other flame-retardants working by other mechanisms.

The heat sink can be provided in the polymer phase (retarding ignition) or in the preheat zone of the flame (weakening the flame). In this way, the effective auto-ignition temperature of a plastic can be raised. An increase in effective heat capacity can be simulated by endothermic components.

There is some reason to believe that endothermically decomposable gases, such as ammonia, even though they can burn, can provide endotherms in the preheat (pre-oxidative) flame zone and thus serve as gas-phase fire suppressants. Additives that evolve ammonia seem to be effective as flame-retardants (Little, 1964; Pitts, 1971; Costa et al., 1991; Cullis et al., 1991; Garo et al., 1992).

The endothermic contribution of volatilized flame-retardants in the preheat and combustion zones of the flame have been given very little notice in the flame-retardancy literature. This neglect is becoming increasingly untenable in the face of some remarkable quantitative calculations, in good agreement with experiment, estimating the efficacy of many flame extinguishants on the basis of mainly endothermic decomposition (Sheinson et al., 1989) or entirely endothermic decomposition (Ewing et al., 1988, 1989, 1994). In a recent development of a computable model for the oxygen index, one investigator found that the model conformed to experiment only if a term was included for endothermic pyrolysis of the vaporized fuel (Búcsi and Rychly, 1992), and the computed oxygen index was quite sensitive to this quantity.

Heat loss not only by endothermicity and heat capacity but also by post-ignition re-radiation is another factor that may be exploited, according to the views of a Russian research group (Khalturinsky and Berlin, 1990). This approach seems to have had very little attention. The Russian workers believe that the reflection or re-radiation of heat may explain the unusual flame-retardant action they found with antimony oxide in a nonhalogen epoxy system.

Taking Advantage of the Damköhler Number Effect: Removing the Fuel from the Combustion Zone before most has Burned

The Damköhler number is a generalized dimensionless variable that can express the ratio of the average retention time of fuel in the combustion zone divided by the average time to undergo combustion. A certain critical Damköhler number must be reached for ignition to occur and another critical Damköhler number must be reached for propagation (Williams, 1974; Sohrab and Williams, 1981). Extinction will occur when the system drops below a critical Damköhler number.

Viewed in terms of the Damköhler number, combustion can be prevented by increasing the denominator (i.e., retarding the rate of the combustion reaction) or by decreasing the numerator (i.e., reducing the retention time of the fuel in the combustion zone). Doing both at the same time gives an even better result.

While inhibiting the rate of the combustion reactions is a familiar strategy, propelling the fuel out of the reaction zone is not so familiar, except incidental to some other function of an additive. We (Zhu et al., 1995) found, much to our surprise, that, in a research project on flame-retarding ethylene-vinyl acetate copolymer, adding a metal nitrate paradoxically gave us a flame-retardant effect. After eliminating other possibilities, we were left with the likely explanation that the sudden surge of carbon dioxide and nitrogen oxides, just before polymer ignition, was perhaps pushing whatever fuel gas was evolved out of the reaction zone before it could be combusted, while also slowing down the combustion rate by dilution of the fuel.

With additives such as melamine, such enhancement of gas evolution would take place concurrently with an endothermic effect. With our nitrate additives, gas evolution is concurrent with an *exothermic* reaction that generates these gases-yet the flame-retardant effect is seen. This curious effect of nitrates probably illustrates flame retardancy achieved by decreasing the Damköhler number.

Shifting Degradation Pathway Away from Volatile Fuel Release to Cross-Linking and/or Generation of Vapors of Low Fuel Value

The more familiar approach of shifting degradation pathway is the likely basis for the highly effective phosphorus-based flame-retardant systems in cellulose; the degradation is shifted from volatile levoglucosan to formation of cross-linked char (Barker and Hendrix, 1979; LeVan, 1984; Lewin, 1984). Enhanced water release is undoubtedly also an important factor. A quantitative study of the thermal effects of flame-retarding cellulose by alkali showed that the reduction of the fuel content of the volatiles counteracted the enhanced rate of degradation and enhanced volatile generation (Chen et al., 1991).

Cross-linking, char enhancement, and water release are probably the main modes of action of phosphorus flame-retardants in certain other systems, for example, in rigid urethane foams. However, phosphorus flame-retardants have several distinct other modes of action, including endothermic effects, radical scavenging effects, and coating effects (Weil, 1992b).

Recent work at the National Institute of Standards and Technology (NIST) provided quantum chemical support to the concept that cross-linking should help flame retardancy (Nyden et al., 1992). However, this idea has for decades been in the "tool kit" of the empirical flame-retardant system designer. It has been well known that the initial formation of thermally stable cross-links begins the process of char formation and retards the formation of volatile fuels (Hindersinn and Witschard, 1978; Brauman, 1979a). For instance, the dechloranes together with certain metal oxides have been known as high-temperature vulcanizing agents for polyolefin elastomers; when they are used as flame-retardants, the result is greatly increased char yield.

This concept has been shown to work with a fairly good range of thermoplastics where there is a functional group that can be exploited for purposes of cross-linking. For example, acid catalysts flame retard PMMA, apparently by causing anhydride links to form, and metal compounds in some cases cause salt cross-links to form (Gruntfest and Young, 1962; Wilkie et al., 1989).

Various other polymer-specific catalytic systems have been found. One example found at Polytechnic University is the action of zinc chloride ($ZnCl_2$) as a catalyst for trimerization of the nitrile group in styrene-acrylonitrile copolymers, with resultant char enhancement (Pearce and Kwei, 1994).

The sulfonate salt flame-retardants, which work at very low levels specifically in polycarbonates, have been shown to be catalysts for the formation of an intumescent char (Ballistreri et al., 1988), although increased carbon dioxide (CO_2) evolution may also have a Damköhler number effect.

Another polymer-specific additive that is almost surely catalytic is platinum used at low levels in peroxide-cured silica-filled silicone rubbers (MacLaury, 1979). The details of the catalytic effect of platinum are not clear, although a French study suggests that it somehow inhibits depolymerization of the siloxane structure (Lagarde and Lahaye, 1977). However, this is one of the most efficient flame-retardant additives known, having a detectable effect at partsper-million levels; and it affords reason for hoping that other such highly efficient catalyst systems may be possible.

Somewhat related to these ideas is the concept of scavenging radicals in the decomposing polymer to perhaps retard decomposition to volatile fuel. At the typical temperatures of burning polymers, above 300 °*C* at least, there are few effective radical scavengers. The classical antioxidants do not work at these temperatures. One of the many proposed mechanisms for red phosphorus, an effective flame-retardant, is radical scavenging in the decomposing polymer phase; the rather weak evidence is that red phosphorus retards pyrolytic degradation of polyethylene (Peters, 1979). There are several other modes of action of red phosphorus and it is difficult to assess the relative contribution of each.

In principle, the radical scavenging approach should work best in those polymers that fragmentize under radical initiation, but the same additives might antagonize flame retardancy in polymers that cross-link with radical initiation. Some marginal flame-retardant effects of antioxidants have been observed (Weil, 1987).

Rapid Formation of Barriers to Heat and Mass Transfer

Any char formation should be beneficial, at the very least by representing material that escapes burning, but the flame-retardant effect of char is obviously greater the better the char layer serves as a barrier to heat and mass transfer and the more quickly it is formed. Intumescent, that is, foamed and expanded, chars are clearly desirable.

The relationship of char yield (as measured by thermogravimetric analysis (TGA) under nitrogen) to oxygen index has been well demonstrated for charrable polymers (Van Krevelen, 1975, 1990), but there are many complicating factors in the relationship of charring when flame retardancy is measured by other means, or with polymers that do not char well.

One important factor in the relationship of char to flammability is the *rate* of char formation. This factor has only recently been noted in flame-retardancy studies (Gnedin et al., 1993). In a recent study done in our laboratory using combinations of two phosphorus-containing additives, one being melamine phosphate and the other being a phosphonate ester, we found a useful synergism; interestingly, the flame retardancy was found to correlate not to the quantity of char but to the rate of char formation (Zhu et al., 1995).

As have earlier workers at American Cyanamid and B.F. Goodrich (Granzow, 1978; Savides et al., 1979; Hall et al., 1985), we at Polytechnic University have found various synergistic combinations of phosphorus compounds by patient trial and error, and we now think that the basis of this useful phenomenon may be involved with rate of char as well as with amount of char.

Another important aspect of char is the nature of its surface. In a recent Russian study, a phosphorus additive was shown to produce a carbonized layer with a smooth metallic reflection in a filled epoxy resin while, without the phosphorus, the surface was visibly heterogeneous (Kodolov et al., 1993). The principal flame-retardant effect of the phosphorus additive expressed itself as a pronounced ignition delay.

Phosphoric or polyphosphoric acid was found to be present in or on the surface of the char from a phosphorus-flame-retarded polymer. This has been proposed to have a protective effect (Brauman, 1977a, b). We have confirmed the formation of a phosphoric acid layer in the UL-94 ignition of a thermoplastic polyester and we found direct evidence for its flame-retardant effect. This is probably an important part of the flame-retardant action of phosphorus additives.

Further Consideration of Charring—Catalysis

Dehydrogenation and oxidative dehydrogenation catalysts are a generic class of additives that a priori should accelerate char formation under oxidative conditions with water as the byproduct. The char would not only have value as a barrier to heat and mass transfer, but its carbon would represent material left unburnt and obviously not contributing to heat release. The heat of combustion of a reaction consuming only the hydrogen of an aliphatic hydrocarbon polymer molecule is only about one-third the heat of combustion of both the hydrogen and the carbon (Weil et al., 1990). The heat of combustion discrepancy gets even greater for high-performance polymers typically having a high carbon/hydrogen ratio.

The literature shows a few possible cases where the catalytic dehydrogenation approach may have actually worked well. For example, polypropylene has been flame retarded with 2 percent chromium introduced as chromyl groups (Chien and Kiang, 1980). Zinc acetylacetonate at 1 percent was shown to make polypropylene self-extinguishing by the D-635 test and increased char formation was exhibited by this system (Cullis and Hirschler, 1984).

Recently, a Japanese company disclosed data in a patent that showed 0.02-0.05 percent of dehydrogenatively active metal-oxide combinations (Cr_2O_3-ZnO, Fe_2O_3-ZnO, or Al_2O_3-MnO) synergized alumina trihydrate (ATH) additives in polyolefins and prevented drip; they proposed a dehydrogenation mechanism (Shinyoji et al., 1987). Another Japanese company disclosed the synergizing of the flame-retardant effect of magnesium hydroxide in ethylene-vinyl acetate copolymer by small amounts of nickel, iron, manganese, or copper compounds, all plausible dehydrogenation catalysts (Kanemitsuya, 1991).

At Polytechnic, we found that iron oxides and various other iron compounds are effective components of flame-retardant systems in certain polyamides (Weil et al., 1991). Char morphology was found to be affected by these iron additives. The char appeared shiny, continuous, and free of cracks. While the mechanism of action has not been definitely determined, we note that iron is associated with dehydrogenative catalysis, but also that pyrolysis of certain polymers containing iron compounds have been shown to lead to strong glassy carbons (Kammereck et al., 1974). The mechanism of our iron effect is still being studied.

Another stoichiometric equivalent to dehydrogenation is oxidation to hydroxy, hydroperoxy, or keto functionality followed by dehydration thereof. This concept of oxidation as a precursor to charring has been discussed by the NIST group (Nyden et al., 1992).

Some experimental evidence is available for the fortuitous occurrence of this sequence of steps: Delobel and colleagues recently presented evidence for the char-forming reaction of polypropylene oxidation products and ammonium polyphosphate in a system where part of the char is formed from pentaerythritol (Delobel et al., 1989). They have evidence for the presence of a phosphoric or polyphosphoric acid coating and possibly for phosphorylated carbonaceous structures (Delobel et al., 1989, 1991).

It would appear timely to explore such flame-retardant applications for dehydrogenation or oxidative dehydrogenation catalysis, since recent progress has been made in this type of catalysis in the petrochemical field. It should be noted that this catalytic chemistry does not require particularly toxic metals or particularly expensive metals; some of the catalysts reported in the petrochemical field are based on zirconium, aluminum, zinc, molybdenum, and iron. Polymer additives based on this type of catalysis seem feasible.

Of course, we cannot be sure that the same catalysts that promote dehydrogenation or oxidative dehydrogenation of small petrochemical molecules will work for polymers in inducing char formation at fire exposure temperatures.

In our own recent work at Polytechnic, we have pursued this working hypothesis and have found some synergistic results of known dehydrogenation or oxidative dehydrogenation catalysts with other flame-retardants, but have not found any manifestation of this effect strong enough to provide us with a "stand-alone" flame-retardant. However, we believe that the advanced thermoplastics should actually respond better to this type of catalytic additive (less heat of combustion to counteract the effect, and inherently higher char yield to assist the effect).

A substantial body of knowledge of carbonization catalysis is available in other fields of technology, such as conversion of coal to coke, production of carbon fibers and electrodes from pitch, and production of carbon-carbon composites. For example, in making chemically activated carbons from wood, it is typical to use zinc chloride or phosphoric acid. In coal liquefaction by pyrolysis, divalent metal cations increase the char/liquid ratio (Whitehurst et al., 1980; Serio et al., 1993). This literature is too extensive to review here. Fuel technology journals often discuss catalytic factors in carbonization chemistry, and this discussion may suggest leads to charinducing polymer additives.

It may be useful to consider the pathways for the conversion of the carbon content of the polymer, first to cross-linked polymer, then to amorphous carbon-rich material, then to partially organized "turbostratic" or "mesophase" carbon structures, and finally to graphitic structures. A laser Raman study at GE showed that the end product was much the same for several polymers but that the intervening steps were different (Factor, 1990).

Much of the literature on carbonization and graphitization deals with the process at temperatures above the likely temperatures of char and at time scales beyond that which we are concerned with in flame-retarding polymers. Nevertheless, there are clues that may suggest useful polymer additives. Boron appears to be a uniquely effective graphitization catalyst in both the turbostratic phase and the graphitization phase (Oya et al., 1979). A wide variety of metals has been shown to have catalytic activity in graphitization (Oya and Marsh, 1982). It was found that the dehydrogenation and carbonization of coal tar pitch can be catalyzed below 700 °C by finely divided molybdenum particles (Ishihara et al., 1993). A study in a Russian petrochemical laboratory (Galimov and Rakhimov, 1990) shows that phosphorus acids can catalyze the condensation of polycondensed aromatic hydrocarbons to form coke.

Besides the carbon structure on the molecular level, the larger-scale morphology is clearly important. The ideal morphology is that of a closed cell foam, as shown by microphotography (Bertelli et al., 1989). Phosphorus additives appeared helpful in this study. We found that iron compounds improved the macroscopic structure of our char from nylon-4,6 with polyphenylene oxide (Weil et al., 1991).

In one recent study on polyolefins with an intumescent flame-retardant additive system, the further addition of SnO_2 (which reacts with the char) was found to cause the char to have an undesirable porous flaky structure, whereas TiO_2, acting perhaps as a binder, was helpful in producing a coherent foam of good insulating character (Scharf et al., 1990).

Special Problems of Catalyst Design and Possible Solutions

The concept of char-promoting catalysts poses a dilemma when one attempts to apply it to polymers. On the one hand, if the catalyst is heterogeneous, polymers are not likely to be able to penetrate more than superficially, and product molecules may not be able to desorb. So a good dehydrogenation catalyst may only produce a local surface char of little protective value and may instantly become fouled.

On the other hand, while homogeneous catalysts might not be expected to have this defect, especially if they can be dissolved in the polymer, such catalysts are fewer, they usually involve expensive ligands, and they are for the most part limited in their thermal stability. A proof of concept is the use of Wilkinson's Catalyst as a flame-retardant for poly(methyl methacrylate), working probably by cross-linking (Sirdesai and Wilkie, 1989). This catalyst is admittedly too expensive and not active enough for real use, but such work stimulates the search for further catalysts and mechanisms of action.

A possible escape from this dilemma is the use of nanoscale catalyst particles, having large surface area, little need for penetration of reactants into their interior, and possibly good thermal stability. A nice prototype for this concept is the recent finding of the effective cross-linking (probable smoke-suppressant) effect in polyvinylchloride of colloidally dispersed copper (Jeng et al., 1994).

Introduction of Polymeric Additives to Provide Char

Although most advanced thermoplastics such as polyetherimides and polysulfones are good char formers in their own right, they could benefit by further increase in char yield and they may likely need improvement in *rate* of charring.

The addition of a good char-forming polymer to a less charrable polymer has been recognized as a valid approach to building a flame-retardant polymer system. One successful prototype is Noryl®, a blend of polyphenylene oxide (PPO) which is a good char former with high impact polystyrene, a poor char former. GE researchers have shown that the char-forming character of the PPO is strongly contributory to the overall flame-retardant effect; it is only necessary to add a moderate amount of an aryl phosphate to overcome the flammability of the pyrolysis products of the high-impact polystyrene component of the blend (Carnahan et al., 1979).

Noryl® contains PPO as a major component. We find that even small additive quantities of PPO, down in the 5 percent range, are quite useful when we are building a flame-retardant system for a poorly charrable polymer such as a nylon or a styrenic (Weil et al., 1991; Weil, 1992b).

The *rate* of char formation seems to have been less studied than the char yield. A recent study at Polytechnic University suggested that rate of char was the key variable in the flame-retardant effect of a series of related char-forming polyphenylene oxides (Zhu et al., 1995). We also found some statistical evidence for different flame-retardant contributions of fast char formers and slow char formers in a study of flame retardancy of styrenics (Weil, 1992b).

We think that it will be found productive to add fast char formers even to those engineering thermoplastics that provide, by themselves, a good char yield. We find fast char formers to include certain novolacs. Some other plausible examples are the special novolac and "cardo" molecules described by Polytechnic University researchers (Lin and Pearce, 1979, 1981a, b; Lin et al., 1981; Lo, 1981; Pearce, 1984).

Introduction of Reactive Cross-Linking Additives

Even if the matrix polymer itself can char, the rate of polymer chain-polymer chain reactions leading to cross-linking may be relatively slow (Arrhenius pre-exponential term may be small) compared to the rate of reaction of some smaller molecule capable of causing crosslinking. Proof of concept was done years ago at SRI (Brauman, 1979b) using xylylene dichloride plus latent Friedel-Crafts catalyst in a styrenic polymer (a poorly charrable polymer that was thus induced to char). Later industrial researchers used less toxic bifunctional benzylating agents (Clubley et al., 1981).

This approach may be somewhat polymer-specific. However, most or all of the high-performance engineering thermoplastics have aromatic groups in their backbone, and in many instances they have rather electron-rich aromatic groups bearing oxygen or nitrogen substituents. Thus, polyfunctional alkylating agents or other types of polyfunctional electrophilic reagents should be able to cross-link these chains. Finding suitable additives of this type is a challenge, because they must not be reactive at processing temperatures but must enter into reaction quickly under fire-exposure temperatures. The delayed action could come from either the reagent or the catalyst.

Some interesting hints and clues may be found in the literature pointing to possible polyfunctional alkylating agents. For example, it was shown that in high-impact polystyrene with an antimony/halogen flame-retardant, polybutadiene acted as an anti-drip agent (Wagner and Joesten, 1976). It is tempting to consider that polybutadiene may have been alkylating the styrenic component. By itself, under these same conditions, polybutadiene underwent reactions suggesting cationic mechanisms.

Improving the Barrier Quality by Introducing Heteroelements

The "char" barrier to heat and mass transfer needs to be coherent, adherent, fast forming, and preferably somewhat intumesced with closed cells, but the barrier material need not be entirely or even primarily carbonaceous.

The efficacy of a noncombustible noncarbon barrier layer was shown some years ago (Ellard, 1973). In this study of intumescent coatings, an advantageous protective effect was obtained when a refractory "char" component remained even if much of the carbon content from the polymer matrix was burned away. Glassy antimonate or phosphate barrier materials were shown to be effective. TiO_2 and mica were also effective. These refractory barriers also had high infrared reflectance. Although this study was directed to coatings, it should be applicable to plastics.

GE has done extensive work in including siloxane units in polymers with resultant formation of improved fire-barrier material. An excellent basic study by Kambour shows that this is a subtle effect with a distinct maximum of flame-retardant performance versus composition. In one study, the peak of flame retardancy coincided with a peak of char strength (Kambour et al., 1981).

It is significant that some recent research at NIST showed that in polycarbonate modified by silicone, while the rate of heat release was greatly reduced, the piloted ignition time was shortened and the flame spread rate was increased. Apparently, the intumesced char did not form fast enough (Kashiwagi et al., 1993).

Some flame-retardant systems with rather low levels of silicone structures as additives have been described by GE authors (Frye, 1984; Schroll and MacLaury, 1984; MacLaury, 1990). A recent example, which showed a very impressive reduction of rate of heat release by levels as low as 1 percent of a silicone additive in polystyrene, was presented by Dow Corning researchers (Page et al., 1993).

Physical Reinforcement of the Barrier

As char (or any other barrier material) forms, it can also build up stresses from shrinkage or stretching and from gases attempting to break out, and it can become cracked or porous. It has been shown (Gibov et al., 1990) that the underlying molten polymer and pyrolysates from the polymer can even come to the surface by capillarity through char. It has also been shown that some additives can aggravate this situation by causing perforations in the char; other additives can give more coherent and smooth char (Scharf, 1992).

To prevent this failure of the barrier, an approach known in the art of fire-retardant coatings is to use "bridging" additives (Anderson et al., 1985). We have found that in thermoplastics, small amounts of high-aspect materials such as mica or wollastonite can help, even in the range of a few percent. We have also seen evidence of synergism between certain high-aspect mineral additives, which we attribute to particularly effective bridging of the char.

We have also noted a small amount of evidence that coupling agents may aid these mineral additives in binding chars (Weil, 1987), although some of the cited effects may have been from improved dispersion. There are even some indications that flame retardancy may peak at some low loading level of coupling agent, so that the effect may require very little coupling agent and thus be economical. There is one Russian report that an elastomer containing an organophilicized clay gave the best flame retardancy and the optimum tensile strength at the same critical loading of surface-modifying agent (Kireenkova and Zuev, 1968).

Preventing Oxidative Destruction and Smoldering of the Barrier

During or after the formation of a char barrier, it can also burn away. The protection of char from smoldering is known to be possible using phosphorus or boron compounds, but this process has not been studied very systematically, nor under high thermal input conditions in regard to flame-retardant plastics. There is a considerable body of knowledge on preventing carbon-carbon composites from burning away at high temperatures; small amounts of boron (as boron oxide) or phosphorus (in the +5 oxidation state) can help. As little as 0.1 percent of a phosphorus containing adsorbate on graphite can reduce the rate of oxidation by 75 percent, so the effect is a powerful one (McKee et al., 1984).

If this effect is to be made use of, optimum boron and phosphorus additives should be sought. Boron and phosphorus compounds cover a wide range in volatility, and some chemical ingenuity may be needed to reduce the volatility losses. In our laboratory, we have studied phosphorus compounds from the standpoint of, on the one hand, release to the vapor phase, and on the other hand, retention in and on the char. We consider that especially interesting phosphorus compounds from the standpoint of nonvolatility are the thermally stable phospham, phosphorus nitrides, and oxynitrides (Weil et al., 1993a, b).

Another approach to preventing the burning away of the char is to produce a ceramic or glassy protective layer. The protection of char is perhaps the most logical use of a low-melting ceramic- or glass-forming component. This approach has been studied in connection with protection of carbon fibers and carbon-carbon composites.

Boron oxide from ammonium borate and boric acid appears protective up to 1000 °C and appears to not only form a coating but actually block the active sites on the carbon where oxygen attack occurs by several mechanisms (Jones and Thrower, 1988, 1991). A wide range of borates, silicates, borosilicates, and other ceramic coatings has been reviewed, as well as the principles governing their performance in protecting carbon at various temperature ranges (McKee, 1986; Strife and Sheehan, 1988; Sheehan, 1990).

In principle, a very-low-melting glass could even offer protection at a pre-char stage. This approach has a long history. British patent 551 (1735!) discloses borates, alum, and other low-melting salts for protecting canvas against fire. The use of low-melting glass-forming salts has been well demonstrated by work done at B.F. Goodrich with glass-forming compositions such as nickel sulfates and ammonium pentaborate (Myers and Licursi, 1985; Myers et al., 1985; Kroenke, 1986). These low-melting glass formulations provided respectably good flame retardancy to a wide variety of plastics. However, these are water-soluble salts. It happens that the same factors that cause a glass to be low melting usually tend to cause it to be water-soluble.

A number of intriguing proprietary fire protective coatings claimed to work at very high temperatures are probably something of this sort-alkali silicates or borates which, after an organic matrix has burnt away, leave a good fire-protective barrier. A number of such compositions, using fusible inorganic materials added to organic matrices, are described in the patent literature. One recent British patent application (Crompton, 1988) manages to name frits, basalt, sodium silicate, ceramic fibers, mullite, etc., for use in phenolics, polyester resins, ethylene vinyl acetate, and a variety of other thermoplastics. The new idea claimed is to use two different frits with different melting ranges.

A recent German patent application refers explicitly to reduced-heat-release and low-smoke aircraft cabin materials and attempts to cover oxides and oxygen acid salts of groups III-V of the periodic table as additives for all possible aromatic thermoplastics. The examples seem limited to antimony oxide and zinc borate, but the claims are remarkably broad (Buchert et al., 1990).

Corning has devised a family of phosphate glasses whose melting range overlaps that of the higher-temperature engineering thermoplastics. They are marketing these glass-polymer blends for high-performance, dimensionally very stable, high-modulus molding compositions (Quinn and Beall, 1992).

ICI has recently introduced CEPREE, a fairly low melting inorganic additive which, after its organic matrix has largely or completely burned out, begins to melt at 350 °C and form a glassy fire barrier that eventually devitrifies and forms a ceramic fire barrier (Smigie, 1992).

Although these glass- or ceramic-forming compositions can afford a high degree of fire protection under high heat load, they would have some inherent problems from the standpoint of aircraft uses. They have rather high densities and perhaps greater rigidity than desired. Impact strength may be compromised. Also, they may not work quickly enough.

Nevertheless, it would seem that these glass-polymer compositions should be added to the fire-retardant compounders' "tool kit" anyway. To overcome the density problem and stiffness, the commercial glass-polymer blends can be considered as a masterbatch and let down to some much lower glass concentration, where the glass will not have to carry the full burden of being the flame-retardant component. Such an additive may very well cooperate with the other flame-retardant components and, in the best cases, may synergize. At the very least, when the formulation has carbonized, the glass should remain to protect the char.

A further approach to low-melting glasses are materials such as amorphous phosphorus oxynitride (Weil et al., 1993a, b), which have a fairly low density compared to glasses containing metals. They can be water resistant (Bunker et al., 1987). These have been only cursorily explored as flame-retardants and are interesting because of their potentially low cost and the possibility that they offer several modes of flame-retardant action. Other clues have been found to low-melting glasses that might be useful in flame retardancy. It was recently shown that zinc borate appears to help the sintering of alumina, giving a better fire barrier than the alumina alone provides (Shen, 1987). Low-melting glasses based on modified zinc borates have been described as low-melting fluxes for porcelain glazes (Jackson, 1989), but seem not to have been explored in flame retardancy.

Smoke Considerations

Through use of polymers that are inherently good char formers along with additives to further improve the flame retardancy by methods other than flame-zone inhibition, smoke should be a minimal problem. Combustion toxicity likewise is not expected to be a major problem for the same reason. Carbon monoxide, formed by the incomplete combustion of any organic material, appears to be the main killer, and its yield is dominantly controlled by fuel/air ratio and temperature (Hirschler et al., 1993). Reducing the amount of material burnt seems to be the key to low-smoke and toxic gas formation.

A particular point of view we think should be kept in mind is that visible smoke, as measured by a photocell, may not represent the true hazard in regard to aircraft cabin safety. Some vapors are perfectly transparent to the photocell, a typical example being acrolein (formed from some organics), but they may prevent vision by being extreme eye irritants and thus inhibit exit from an aircraft cabin.

Formulating a Flame Retardancy and Smoke Suppression "Package"

The large number of different modes of action for flame-retardants (and smoke suppressants) has the practical importance that these modes can be combined, frequently with additive results, and in quite a few cases with synergistic results (Weil, 1975, 1992a).

Building up a flame-retardant/low-smoke formulation by using combinations of the available "tools" is facilitated by modern software for experimental design and formula development. A combination of theory, working hypotheses, and statistically planned experimentation seems to us to be the most cost-effective way to meet any advanced performance goal.

The Structural Aspect of Flame Retardancy-Layer Effects

Aircraft manufacturers are accustomed to using multilayered panels. It may be sufficient to have one layer that is extraordinarily fire-resistant, provided that the other layers do not defeat this effect. By the strategy of using a "super-f.r. layer," the desired mechanical, aesthetic, and processing properties of the overall structure need not be unduly sacrificed. Any compositions that the proposed research program develops obviously need to be tested in layered structures with other likely materials.

SUMMARY

As an alternative or as a supplement to finding totally new advanced polymers, it seems to us that an effective strategy for attaining very high-performance goals is to try to enhance the performance of the best plastics, or even the "next best" plastics, through use of relatively low levels of functional additives. The use of multiple additives with differing but cooperating modes of activity in optimized combinations found through experimental design seems likely to be productive.

Additive types are suggested based on reflectance, endothermicity in the condensed phase, endothermicity in the gas phase, inert gas emission, inhibition of decomposition reactions, char quantity enhancement, rate of char enhancement, char strengthening, catalysis of pre-char chemistry, cross-linking, formation of solid noncarbon barriers, enhancement of the strength of carbonaceous and noncarbon barriers, coating of char, and inhibition of the oxidation of carbonaceous barriers. There is some precedent for each of these actions, and optimized combinations of these actions should be possible.

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An Overview of Inorganic and Organometallic Polymers

Martel Zeldin[*]

INTRODUCTION

The chemistry and technology of polymeric materials have had a major impact on all facets of our life and the economy of the world. Competition among nations for leadership positions in the development of materials science and technology is economically driven. In fact, it can be predicted that the countries with the most advanced and sophisticated materials technology will offer their citizens the highest standards of living and the greatest hope for national security in the decades to come.

In spite of the importance and widespread use of organic polymers, increasing attention has been given to macromolecules that contain metals and metalloids, that is, inorganic and organometallic polymers. The reasons for the growth in these "hybrid" species are linked to need. For example:

- Organic polymers are often susceptible to reaction with oxygen and ozone. The presence of metals or metalloids reduces that propensity.
- Organic polymers thermally decompose to volatile materials that burn; the presence of inorganics increases thermal stability, reduces inflammability of the volatiles, or increases nonvolatile residues.
- Organic polymers degrade when exposed to ultraviolet and higher energy radiation; inorganics are less susceptible to radiative degradation.
- Organic polymers are somewhat more soluble or swellable in solvents.
- Inorganics generally form stronger bonds and offer greater resistance to free radical cleavage reactions than carbon compounds.
- Longer bond lengths and higher valencies give rise to greater torsional mobility and thus greater flexibility and other dynamic-mechanical properties.

MAJOR CLASSIFICATIONS OF INORGANIC AND ORGANOMETALLIC POLYMERS

Although many elements (metals, semimetals, and nonmetals) have been incorporated in one manner or another into an inorganic and/or organometallic polymer unit, certain elements lend themselves better to products with commercial potential. Thus, for example, silicon containing polymers are used extensively for industrial and consumer products, whereas boron containing polymers (i.e., as prepolymer for boron nitride (BN) ceramics or as carborane

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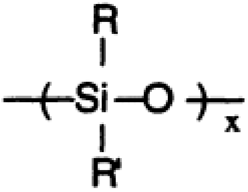
siloxane ultra-high-temperature elastomers) are produced in limited quantity for very special applications. The following is a brief discussion of some of the more important and interesting inorganic and organometallic polymers. Although commercialization has been attained only in a few examples, the potential for design of materials with unusual and significant properties is unlimited.

Silicon-Based Polymeric Materials

Polysiloxanes



$$-\!\left(\overset{\displaystyle R}{\underset{\displaystyle R'}{\mathrm{Si}}}-\mathrm{O}\right)_{x}\!-$$

R = H, hydrocarbon

Polysiloxanes (PSs), compounds containing Si-O bonds in the polymer backbone, are the oldest and largest class of inorganic-organometallic polymers of commercial significance (Rochow, 1987). Worldwide production amounts to about 0.5 million metric tons, with commercial value exceeding $3.5 billion. Their physical properties (see Table 1), which are sufficiently different from those of organic polymers, continue to catch the attention of academic scientists and industrial research and development laboratories. Thus, the growth and development of this class of polymer have remained unabated. In fact, a review of the current literature reveals an increase in the number of publications about and patents for PSs throughout the world. Some of the reasons for the remarkable and sustained growth in this area are:

- The raw materials, principally silicon dioxide, methylchloride and other organic compounds, for the production of PSs are readily available.
- Consumer and industrial applications of PSs are found in commodity and other industries, for example, the plastics, rubber, paper, coatings, automotive, construction, food, biomedical, cosmetics, and specialty chemicals industries.
- PSs' copolymers can be prepared for tailoring physical, dynamic-mechanical, and chemical properties of materials.

What is on the horizon for PSs? Some of the significant developments in the field are summarized below:

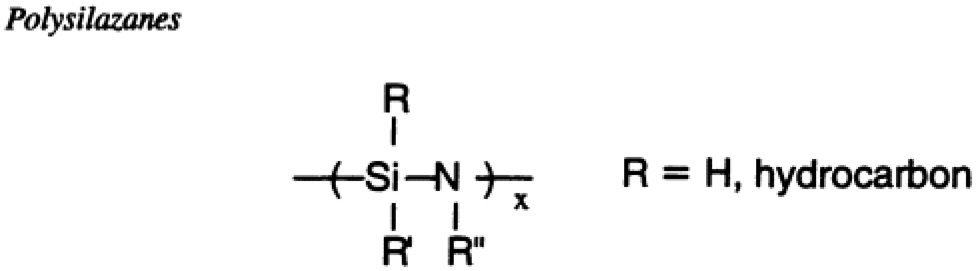
- Recent progress in understanding the mechanism(s) of PS polycondensation and ring-opening polymerization will permit the synthesis of linear polymers with regio and stereoselectivity. Synthetic control of these materials will inevitably lead to dominion over polymer microstructure and hence macroscopic properties (Chojnowski, 1993).

- Advances in methods for copolymer synthesis, both siloxane-siloxane (Kennan, 1993) and siloxane-organic (Smith et al., 1992) polymers, offer greater flexibility in modifying and improving properties for specific applications.
- New functionalized polysiloxanes enable the formation of miscible polymer mixtures and polymer blends for improved properties (Lu et al., 1993).
- Controlled synthesis of cross-linked network PSs, for example, silsesquioxanes and related copolymers (Lichtenhan et al., 1993), interpenetrating networks (U.K. Patent 804,199; U.S. Patent 3,971,705; Lestel et al., 1990), and hyperbranched hybrid PSs (Rubinsztajn, 1994; Rubinsztajn et al., in press), has led to materials with significantly improved thermal, mechanical, and optical properties.
- Development of the colloid chemistry of silica (sol-gel processes and technology) has had a significant impact on the preceramic, ceramic, and surface coatings industry (Brinker et al., 1988; Huang et al., 1988; Sakka et al., 1988; Schmidt, 1988; Bergna, 1994).

TABLE 1 Some Properties and Major Uses of Polysiloxanes

Properties	Uses
Low glass transition temperature	Heat exchange fluids
Low thermal coefficient of viscosity	Dielectric fluids
High thermal stability	Antifoams
Oxidative stability	Lubricants
Hydrophobicity-lipophilicity	Polishes
Elasticity	RTV and HTV rubbers
Low surface energy	Chromatographic resins
Biological inertness	Refractory materials
Photochemical stability	Damping fluids
Low dielectric constant	Biomedical applications

Polysilazanes

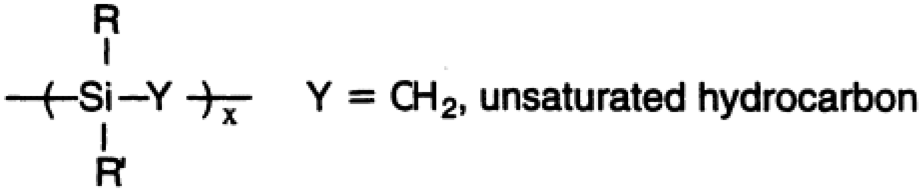


$$-\!\!\left(\underset{R'}{\overset{R}{Si}}-\underset{R''}{N}\right)_x\!\!-\qquad R = H,\ \text{hydrocarbon}$$

Polysilazanes, compounds containing Si-N bonds in the polymer backbone are an example of organometallic precursors to advanced non-oxide ceramic materials, for example, for reinforcement of ceramic, plastic, and metal matrix composites (Zeigler and Fearon, 1987). Such ceramic materials offer a wide variety of unique physical properties that include extreme hardness, high structural and thermal stability under extremes of environmental conditions, and potential for electronic and optical properties. The major challenges facing further commercialization of polysilazanes and ceramic progeny are the following:

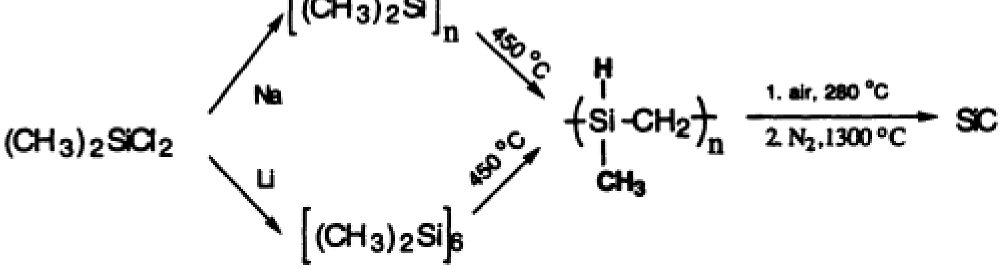
- synthesis of tractable prepolymers, that is, precursors with solubility in common organic solvents;
- precursors with sufficiently high molecular weight or optimum degree of crosslinking for shape retention in the pyrolytic process of ceramic formation;
- ability to attain high ceramic conversion;
- control of the pyrolysis process to minimize ceramic porosity; and
- reduction of carbon content in the ceramic product.

Polycarbosilanes



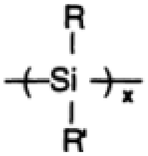
$$-\!\left(\overset{R}{\underset{R'}{Si}}-Y\right)_x\!-\quad Y = CH_2\text{, unsaturated hydrocarbon}$$

Like polysilazanes, polycarbosilanes, compounds containing Si-C bonds in the polymer backbone are an example of organometallic precursors for advanced silicon carbide (SiC) ceramic materials. Their route through polysilanes has been commercialized by the Nippon Carbon Co. into silicon carbide fibers (NICALON^{TM}) (see scheme below).



SiC-based ceramic materials offer a wide variety of physical properties that include extreme hardness, high structural and thermal stability, and future potential as coating materials for electronic and optical devices. Recently, novel carbosilane dendritic macromolecules have been prepared (Zhou and Roovers, 1993). These starburst-hyperbranched polymers are three-dimensional symmetric species with well-defined 32- and 64-arm structures of intermediate molecular weight. These materials may have interesting physical properties. Additionally, stable comb-like polymers with carbon unsaturation in the polymer backbone and pendant oligo(oxyethylene) units have been synthesized (Wang and Weber, 1993; Chen et al., 1993). Significantly, ceramic materials from their pyrolysis have high char yield. The combination of solubility and hydrolytic and thermal stability of these polycarbosilanes offers opportunities to tailor properties by using appropriate preceramic polymer blends. Similarly, new branched polyhydridocarbosilanes are precursors to high-residue (> 70 percent) SiC ceramics (Froehling, 1993). Patents for these materials are in progress.

Polysilanes

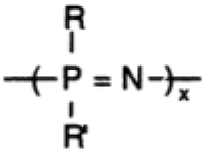


$$\left(\begin{array}{c} R \\ | \\ -Si- \\ | \\ R' \end{array}\right)_x$$

R = Organic

Although polysilanes, compounds with Si-Si bonds in the polymer backbone, have been known for decades, only recently has synthetic methodology been sufficiently perfected to afford soluble oligomers and high molecular weight polymers that can be fully characterized. These substances are stable to 300 °C, mildly susceptible to hydrolysis, and, contrary to early predictions, inert to oxygen at ordinary temperatures. Perhaps the most significant and surprising discovery is that these materials possess interesting and commercially important photochemical and electronic properties. For example, since poly(diorganosilane)s absorb light in the visible and ultraviolet region of the spectrum as a function of substituent and chain length, and photodecay to volatile products, they have great potential as positive photoresists in the microelectronics industry and photoconductors in the electrophotography industry. In addition, they serve as free radical photoinitiators in organic reactions and display nonlinear optical properties for potential use in lasers and other optical devices (Mark et al., 1992).

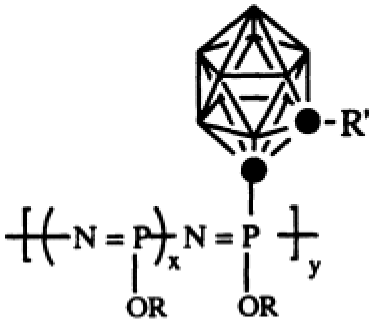
Phosphorous-Based Polymeric Materials



$$\left(\begin{array}{c} R \\ | \\ -P=N- \\ | \\ R' \end{array}\right)_x$$

R = Just about any type of substituent

Polyphosphazenes, compounds with P-N bonds in the polymer backbone is rivaled only by polysiloxanes with respect to diversity of species and potential for commercialization. The potential for growth and development of this unusual class of materials is reflected in the synthetic ease with which framing substituents, R, can be changed and modified, and in the consequential variations in physical and chemical properties that occur from the compositional versatility (Allcock, 1988; Allcock et al., 1992). Thus, different pendant groups lead to dramatically different materials, that is, elastomers or glasses, hydrophobic or hydrophilic polymers, inert or highly reactive materials, insulators or conductors, photoactive or photoinert materials, and bioerodible or bioinert material. Table 2 summarizes some of the current and projected applications of polyphosphazenes. Some unusual polyphosphazenes are noted below.



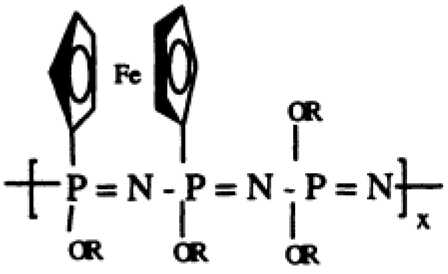


TABLE 2 Applications of Polyphosphazenes

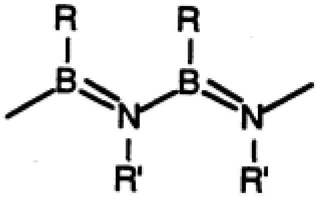
Elastomers
Ionic electrical conductors
Membranes
Water repellents
Nonburning textile fibers
Foam heat and sound insulators
Hydrocarbon solvent-resistant O-rings and gaskets
Immobilized enzymes
Controlled drug-release agents
Hydrogels for prostheses and soft-tissue applications
Liquid crystalline polymers for nonlinear optical properties
Ceramics

Although other inorganic and semi-inorganic polymers containing phosphorus (e.g., phoryl resins, poly (alkylene phosphates), polycarbophosphazenes) are known and, in some instances, possess interesting properties (transparency, hardness, flame retardancy, adhesion, biocompatibility, and elasticity), they appear to suffer from three major disadvantages—high cost, oxidative instability, and hydrolytic sensitivity. Perhaps further research on related compositions will produce new classes of materials without the problems.

OTHER TYPES OF INORGANIC AND ORGANOMETALLIC POLYMERS

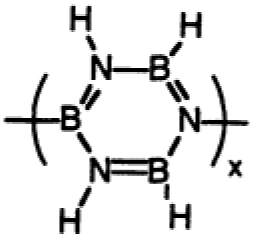
Boron-and Aluminum-Containing Polymers

Polyborylamines and Polyborazines

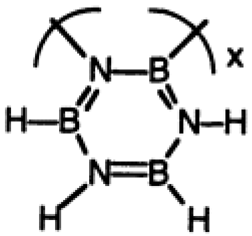


R = Hydrocarbon

1



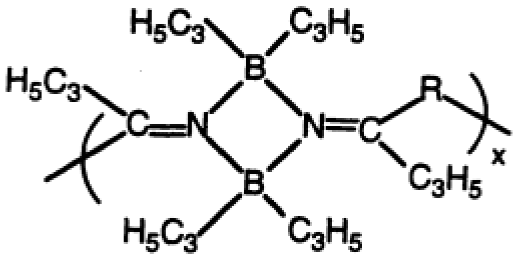
2a



2b

Polyborylamines (1) and polyborazines (2a, 2b), compounds with the B-N bond in the backbone as linear chain, or connected 1,2 or 1,6 six-member rings, are precursors to non-oxide BN ceramics. Like the SiC, silicon nitride (SiN), and boron carbide (BC) materials, BN ceramics are of great interest due to their exceptional hardness and stability to oxygen and water under extremes of conditions. The use of BN ceramics as coatings, reinforcing fibers, and new generation composite materials depends on the ability to produce readily processible polymers and prepolymers that can be shaped or spun into filaments before pyrolytic transformation into products. A considerable amount of effort has been expended in several laboratories, both here and abroad, in the search for soluble, processible polymers. Some success has been reported over the past decade (Narula et al., 1988; Paciorek et al., 1988; Shaw et al., 1988); however, the field needs considerably more research and development support.

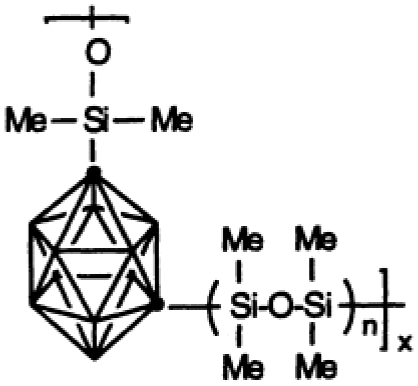
Hybrid Boron-Nitrogen-Carbon Polymers



$R = C_6H_4, (CH_2)_n$

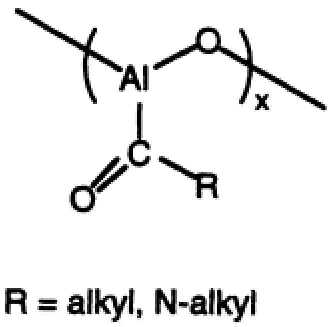
A new class of soluble boron-nitrogen-carbon (BNC)-containing polymers, prepared by allylboration polymerization, has recently been reported (Chujo et al., 1992). Relatively lowmolecular-weight (M_n, 5,000-14,000), organic soluble oligomers in pure form are obtained and have been fully characterized. Although pyrolysis of the polymer at 900 °C gives a BNC ceramic-like material, the properties of the product have not been published.

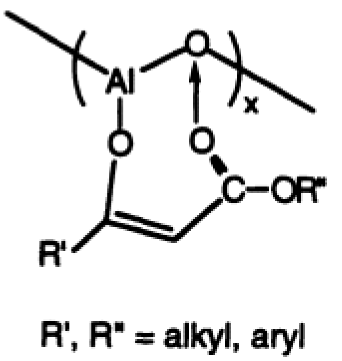
Carborane Cage Polymers



Synthesis of m-carborane cage polymers based on the decaborane cage structure, $CB_{10}H_{10}C$-, was achieved in the 1960s (see Allcock and Lampe, 1990). Incorporation of poly(dimethylsiloxyl) units between the cage functions results in elastomeric copolymers that retain their thermal stability ($T_d > 500$ °C), low T_g (-30 °C), and chemical-oxidative stability. These properties lead to high-performance applications as specialty (Dexil) resins for chromatography. Related materials, which contain diamine groups, have resulted in BN-like fibers. Although these substances were studied extensively in the 1960s and 1970s, further development of them has essentially ceased due to the difficulty and cost of producing the parent carboranes.

Oligo (aluminoxane)s

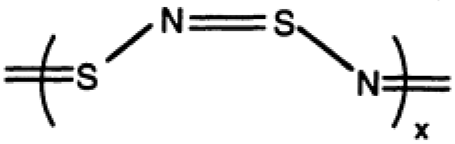




Oligo(aluminoxane)s, prepared by condensation polymerization of $AlCl_3$ in the presence of aqueous organic acids or amides, are low molecular weight, highly branched, soluble materials with the A1-O bond as the basic repeat structural unit. These compounds have found application as "drag-reducing" agents for fluid (oil or water) flow, drying and gelling agents, coatings, fuel additives, catalysts, and lubricants. These oligomers and the amide analogs can be melt-spun into fibers that, upon pyrolysis, yield Al_2O_3 (alumina) and A1N (aluminum nitride).

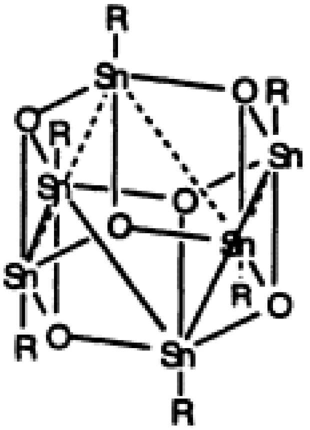
Sulfur-Containing, Polythiazyl (S-N)x, Polymers

Sulfur-containing polymers have been studied for decades. Elemental sulfur itself is a polyatomic, polymorphic material, and exists as chains and rings (i.e., S_6, S_8). Although the element is low in cost and plentiful, there was only intermittent research and development activity until the 1970s.

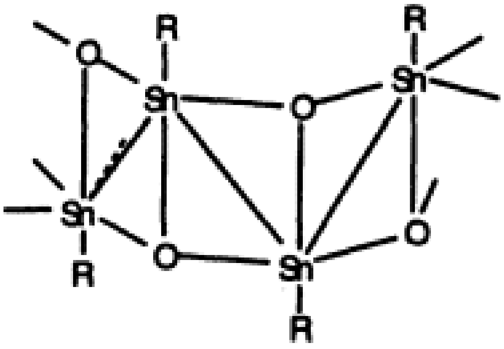


In 1975, the spotlight was turned onto S-N polymers because of their remarkable metal like appearance and their properties, for example, malleability, electrical conductivity, oriented epitaxial structure, optical polarizability, and superconductivity (at 0.3 °*C)* (Mikulski et al., 1975). The polymer can be fabricated as thin films on glass or synthetic polymeric surface by epitaxial polymerization. They have a gold color by reflected light and blue color by transmitted light. They are "relatively" inert to air and moisture; however, they detonate on compression and depolymerize under ambient conditions on long standing. Polythiazyls are the forerunners of polyacetylenes.

Tin-Containing Polymers



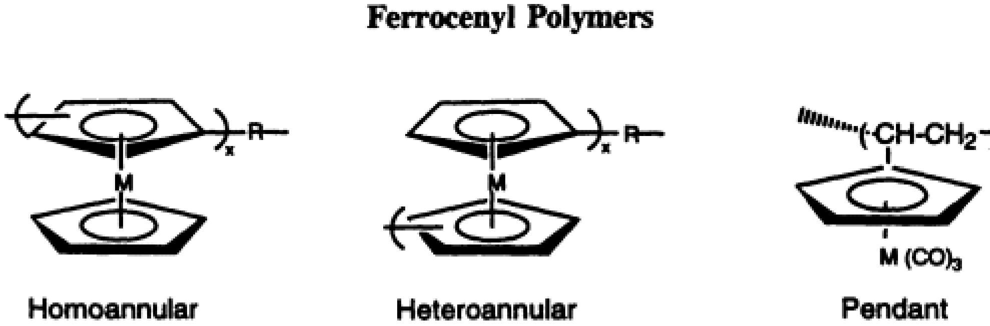
Drum



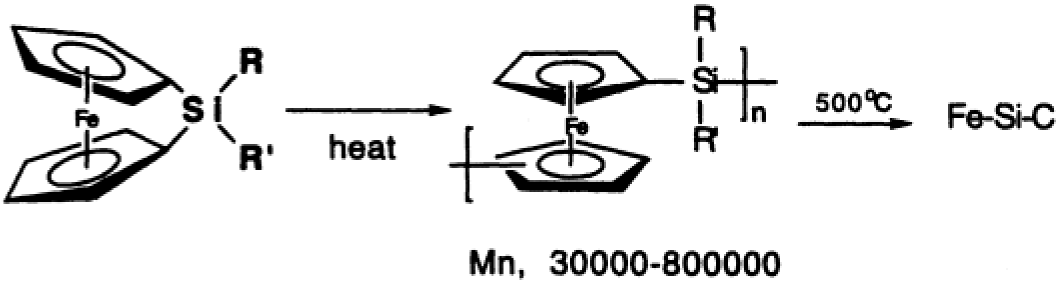
Ladder

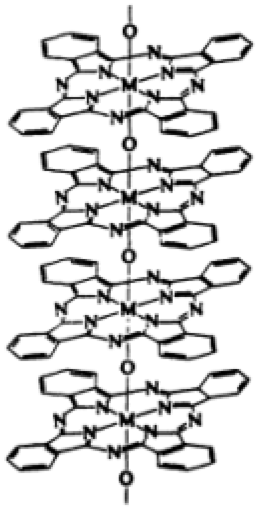
Most notable of the tin-containing macromolecules are the ladder-like polymers. Interest in these materials is relatively recent and a result of their high temperature stability. Moreover, it has been found that these stannsequioxanes exist in several structural types ("ladder," "drum," and "butterfly") and contain hypervalent tin (Holmes et al., 1988). The biological activity of tin species has discouraged their continued investigation as commercially useful materials.

Ferrocenyl Polymers



Metallocenyl polymers, which contain a wide variety of metallic elements, have been known for a long time. Most of the studies on these materials occurred in the 1960s, principally with iron as the metal center (Neuse, 1982). The structural units depicted above (homoannular, heteroannular, and pendant) represent only a few of the types that have been synthesized. The major limitations in further development of homo- and heteroannular materials results from low solubility, low-to-moderate molecular weights, and lack of mechanical properties for applications. Recently, pendant-type water-soluble polymers, such as polyaspartamide-bound ferrocene compounds, have been prepared and characterized. These materials were found to have salient biomedical applications (Neuse et al., 1990). A strained-ring ferrocenyl-silane (below), which can be thermally polymerized to an amorphous magnetic iron-containing SiC ceramic, has been recently reported (Manners, 1993).

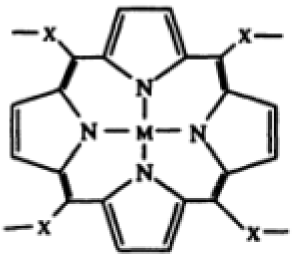




Phthalocyanine (shiskabab) Polymers

Phthalocyanines are planar macrocyclic rings composed of aromatic groups and nitrogen atoms capable of tetra coordination with a metal or metalloid. Polycondensation of a monomeric diol derivative, where M = Si, Ge, or Sn, leads to one-dimensional stacked metalloxy chain macromolecules with unusual physical and dynamic-mechanical properties. These polymers dissolve in strong acids and are spinnable into fibers. Since they are highly oriented, they can be co-spun with such materials as polyaramids (e.g., Kevlar®) to impart strength and thermal stability. Moreover, upon doping with iodine, before or after spinning, the phthalocyanine polymers possess interesting magnetic and electronic (conductor and semiconductor), as well as optical, properties (Marks et al., 1988).

Metalloporphyrin Polymers



M = Fe(III), Co(II), Ni(II), Zn(II)
X = Organic function

Metalloporphyrin polymers have been popular recently due to potential catalytic, electrochemical, and electrical-photonic properties. For example, work by Lindsey and colleagues has demonstrated that, with M = Zn and the appropriate in-chain polymer spacer groups, an oligomer can act as a 9-nm macromolecular photonic wire with 76 percent energy transfer efficiency (Wagner and Lindsey, 1994).

SUMMARY

Research on inorganic and organometallic polymers has grown enormously over the past 30 years. The above overview represents a relatively small perspective of the breadth and scope of the field that has taken numerous, interesting diversions based, on the one hand, on intellectual curiosity and creativity, and on the other, on economic objectives. As long as special properties and function are desired, new organic, inorganic, organometallic, hybrid materials will be discovered.

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Flame-Retarding Wool Textile Materials and the Evaluation of Thermally Stable Polymers for Commercial Airplanes

*Sally A. Hasselbrack**

ABSTRACT

Current methods of flame-retarding wool fibers and the rationale for selecting the low-smoke zirconium finish as the basis for decorative applications used within the airplane cabin are discussed. Upholstery and drapery applications for using flame-retardant washable wool is outlined with recommendations for its usage. An overview of the Boeing methodology for evaluating the inherently flame-retardant and thermally stable polymers with their possible application is presented.

INTRODUCTION AND HISTORICAL OVERVIEW

The selection of interior textile materials for commercial airplanes that are light in weight, possess the desirable in-service use characteristics, and incorporate all the aspects of fire safety provides a challenging opportunity to incorporate the latest technology into the mainstream of commercial production.

The Boeing 757 and 767 models were the first to include design guidelines stipulating the incorporation of materials with limited smoke and toxic gas emission wherever possible. These 1976 guidelines are found in Table 1. Prior technology incorporated the use of polyvinylchloride (PVC) fiber in the warp and a phosphorous-based flame-retardant (FR) finish on the wool filling yarns as the primary flame-retardant system for upholstery and drapery. Concurrently with the design guidelines, a publication from the International Wool Secretariat (IWS) in the United Kingdom described laboratory research utilizing zirconium and titanium compounds for flame-retarding wool (Benisek and Phillips, 1977b, c). The attributes found only in the zirconium finish were (a) white or pale shades were not altered by the FR finish, and (b) the finish was adaptable to a low-smoke version, termed "Zirpro."

With the cooperation of the Boris Kroll Company, Boeing entered into a small, proprietary pilot study incorporating the low-smoke Zirpro finish in a commercial production environment. All of the development work was done on the 757 and 767 flight deck upholstery because it was the one upholstery remaining constant throughout both programs. The low-smoke zirconium finish was compared at two pH and add-on levels. The pilot program clearly demonstrated that the amount of nylon in the blend was more sensitive in a production environment than demonstrated in laboratory findings. The critical findings were (a) the finish was capable of withstanding 10 dry cleanings, although, a nylon content exceeding 10 percent

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* Boeing Commercial Airplane Group, Seattle, Washington.

TABLE 1 Design Guidelines for Boeing 757 and 767 Models, 1976

Smoke generation at 4 min					
D_s <50				large areas[a]	
<200				small areas	
Toxic gas emission at 4 min					
Draeger tubes					
CO	HCN	HF	HCl	SO_2	NO_x
3,500	150	50	500	100	100
flame spread index[b]					
I_s <25					
Vertical burn[c]					
12-signition, vertical orientation-all textile materials					
60-signition, vertical orientation-textile wall applications					
bonded to panel					

NOTE: Smoke and toxic gas emissions evaluated in the NBS Smoke Chamber at 2.5 W/cm², flaming mode

[a] Large area is greater than 100 sq. in.

[b] flame spread index pertains to all panel constructions, passenger service units, cargo liners, floor panels, floor beams, and acoustic and thermal insulation.

[c] Federal Aviation Regulation 25.853 Amendment 32.

compromised the number of dry cleanings; and (b) the FR finishing bath was very sensitive to slight deviations in the quantity and type of acid used and to the pH level of the bath. Based on the results of this study, Boeing Materials Technology recommended that the upholstery/drapery suppliers utilize the low-smoke Zirpro treatment and limit the nylon content to 10 percent.

Table 2 and Figure 1 illustrate the quantity and the sequence in which the chemicals are added to the finish bath and the recommended time/temperature profile for their application. The Federal Aviation Administration regulation pertaining to carpet and drapery is a 12-second vertical Bunsen burner test. Upholstery is required to pass the Bunsen burner and the oil burner tests (see below).

TABLE 2 Low-Smoke Zirpro Treatments for 100 Percent Wool Upholstery and Carpets (in percent)

	Upholstery	Carpets
Formic acid (90%)	10.0	10.0
Citric acid monohydrate	6.0	8.0
Potassium hexafluorozirconate	3.5	2.3
Zirconium acetate solution (22% ZrO_2)	7.7	10.0

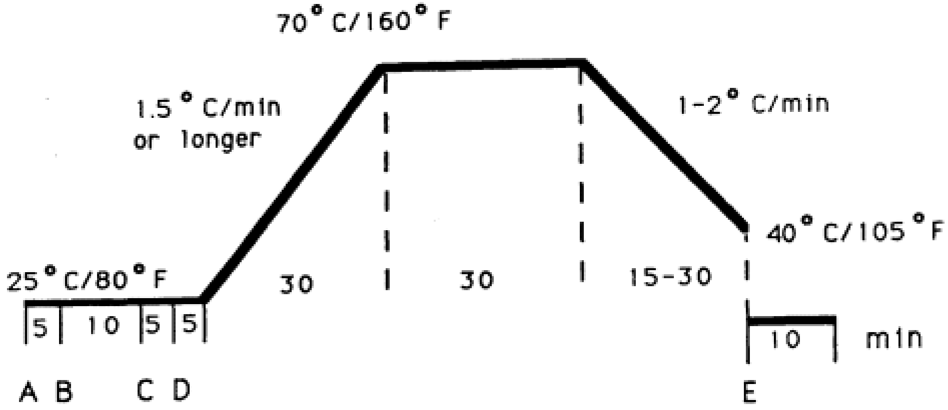

FIGURE 1 Application procedure for low-smoke treatments of 100 percent wool.

FIGURE 1 Application procedure for low-smoke treatments of 100 percent wool.
Step A: 0.1 g/l non-ionic wetting agent, if required. Step B: 10 percent formic acid, x percent citric acid. Step C: y percent potassium hexafluorozirconate (dissolved). Step D: z percent zirconium acetate solution (diluted with cold water) (bath will become cloudy; it will clear as the temperature reaches 45-50 °C). Step E: rinse for 10 minutes in cold water (do not use overflow rinsing).

EFFECT OF THE SEAT FIRE-BLOCKING REGULATION

The regulation credited with saving the most lives in post-crash fires has been the 1984 Seat Fire-Blocking Regulation, Federal Aviation Regulation (FAR) 25, Appendix F, Part II, effective November 1987. This regulation was a quantum step forward in flammability testing, for the following reasons:

- It used a more realistic ignition source to initiate combustion simulating a post-crash fire (oil burner-2-minute ignition at 1800 °F, minimum).
- It was the first regulation for airplane interiors to evaluate materials in their composite form.
- It mandated retroactivity for the entire fleet.

In the initial phase, almost all of the fire-blocking layers were woven or needled blends of polybenzimidazole (PBI) Nomex/Kevlar in varying ratios. Two other fiber blends also meet the regulation but do not hold up in service, a spun-laced aramid and a preoxidized carbon/aramid blend. At present, two types of FR foam permit most wool upholstery to pass the test without the need for a blocking layer.

WOOL FLAME-RETARDANT TECHNOLOGY FOR LOW HEAT RELEASE APPLICATIONS

Textile products applied to vertical surfaces (i.e., riser/dado panel and wall tapestries) were included in FAR 25 Amendments 61 and 66, pertaining to low heat release. To meet this requirement, a tetrabromophthalic acid (TBPA) treatment is used in combination with the Zirpro treatment. The success of the TBPA treatment is due to the synergism between the zirconium finish, which works in the solid phase, and the organobromine acid, which works in the vapor phase. Initially the IWS (International Wool Secretariat) recommended two forms of the TBPA compound: Apex 160, an emulsified paste with a 40 percent bromine content, and FR 756, a liquid form of disodium salt of TBP anhydride with a 15 percent bromine content. *Zirproflame retardant treatments* references only the FR 756 from Great Lakes Chemical. Table 3 and Figure 2 identify the FR formulation, the sequencing of the flame-retarding chemicals, and the suggested time/temperature model.

As of this writing, the Boeing company is nearing the end of a test program using various chemical ratios in the TBPA finish in combination with different backcoating systems to reintroduce wool as the riser material. Collaborative work with a vendor and an FR finisher for over 1 year has sought to identify a formulation that is repeatable and reduces both the heat release and the smoke numbers to a level that makes the fabric suitable for all panel constructions where the riser fabric can be placed. Two wool constructions have been identified:

TABLE 3 Treatment for Wool-Rich Materials Required to Meet the Ohio State University Rate of Heat Release Test (in percent)

Formic acid (90%)	18.0
Citric acid monohydrate	6.0
Potassium hexafluorozirconate	3.5
Zirconium acetate solution (22% ZrO_2)	7.7
FR 756	10.0

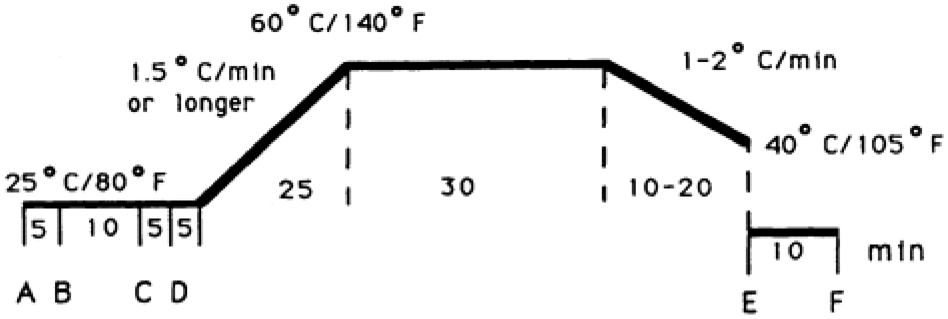

FIGURE 2 Application procedure for low-smoke Zirpro + FR 756 treatments of wool-rich blends to meet the Ohio State University heat release test.

Step A: 0.1 g/1 non-ionic wetting agent, if required. Step B: x percent hydrochloric acid, 6 percent citric acid. Step C: 3.5 percent potassium hexafluorozirconate (dissolved). Step D: 7.7 percent zirconium acetate (diluted with cold water) (bath will become cloudy; it will clear as the temperature reaches 45-50 °C). Step E: y percent FR 756 (dissolved in cold water). Step F: rinse for 10 minutes in cold water (do not use overflow rinsing).

a repp weave with 100 percent wool wrapped around a Nomex core with a Nomex filling yarn; and a low-level-loop grospoint construction of 100 percent wool face pile with a Kermel/Panox backing yarn system. For wall mural/tapestry applications, the only TBPA-treated wool fabric identified to date is the grospoint.

Grospoint material does not have the design capability (long fibers in multiple yarn counts and complex patterns) the Boeing design staff prefers. Test results in Table 4 show that the ratio of cut to loop cannot exceed 40 percent without exceeding the pass/fail criterion of 65/65; and jacquard patterning is not possible (Hasselbrack, 1990). The application of a thin aluminum foil between the fabric and the panel, or some other "work-around," might somewhat expand the patterning capability, but such remedies would not meet the needs of the design staff.

TABLE 4 Heat Release and Smoke Data for Textile Wall Applications

	Heat Release		Smoke
Construction	2-min, kW min\m²	Peak, kW/m²	D, at 4 min
100% P-84 grospoint, low-level loop	13	43	12
100% wool-face grospoint Kermel/Panox backing yarns, all loop pile	31	37	85
100% wool-face grospoint Kermel/Panox backing yarns, 50% cut-50% loop	36	33	122
100% wool-face grospoint Kermel/Panox backing yarns, all cut pile	52	48	161
100% wool-face grospoint Kermel/Panox backing yarns, jacquard pattern, all loop	52	60	192
Replin-100% wool wrap Nomex core, Nomex filling	43	53	141

NOTE: Application is to 0.437-inches-thick graphite phenolic sandwich panel.

WASHABLE FLAME-RETARDANT WOOL

The utilization of TBPA is also an essential part of the FR washable wool program, the latest area of interest within the Boeing company for new flame-retardant developments associated with wool. When the IWS, located in Ilkley, West Yorkshire, United Kingdom (officially renamed Wools of New Zealand in July 1994), first announced a washable FR wool about 10 years ago, Boeing Materials Technology (BMT) tested their submitted yardage. At that time, shrinkage after the first laundering approximated 5-7 percent, and there was minimal progressive shrinkage. With the strong correlation between dimensional stability and abrasion or "wear," Boeing did not recommend the finish without a yardage wet-out prior to the cutting and sewing process. However, as more Boeing 737s were sold to emerging countries, Boeing received requests for an FR washable wool finish. Boeing's Payloads Furnishings contacted several IWS branches around the world requesting an improved finish that would meet the shrinkage and appearance requirements of the airline industry. The U.K. branch, working in connection with all the traditional Boeing suppliers, initiated a new study to significantly reduce the shrinkage problem while maintaining a goal of 15 launderings and 2 percent change in dimensional stability.

Wools of New Zealand (WNZ) states that any type of shrink-resist process must be compatible with the Zirpro process because *it is the only* flame-retardant treatment for wool durable to washing. Their suggested options for the shrink-resist treatment of wool include (a) chlorine/Hercosett, an established process applied to the fiber in the worsted tops form; and (b) the combination of two polymers, Synthappret BAP/Neoprene 400, applied in equal amounts to the woven, dyed fabric by a padding process. With either method, the flame-retardant finish is applied *after* the shrink-resistant finish. As of this writing, some of the WNZ technical staff state a preference for the BAP process due to better appearance retention and abrasion resistance as measured by Martindale. It is expected that the BAP process would be slightly more expensive because more processing steps are required. The technical literature states that the standard zirconium finish is less durable in combination with the shrink-resistant treatment than is the low-smoke version, and recommends the FR 756 to enhance washing fastness (WNZ, 1994).

Test data showing burn length and extinguishing time as related to the number of launderings are available. A brochure supplied by WNZ specifies in some detail the finish application and the precise laundering instructions. With this information, interested carriers can obtain samples of fabric with the FR washable finish and conduct internal tests to ensure their wool material is conducive to the procedures to which the fabric will be subjected.

The WNZ recommends that the weight of the fabric not fall below 11 oz/yd^2, as they have found that the number of washing cycles is related to the fabric weight. Additional guidelines regarding the types of material that are suitable for the additional processing include:

- at 11 oz/yd^2, only 100 percent wool should be considered; and
- both the shrinkage and appearance retention are improved with a tightly woven fabric.

At 14 oz/yd^2 WNZ finds that

- the materials can withstand up to 19-20 launderings;
- the number of launderings can be extended if 100 percent wool is selected; and
- 10 percent nylon can be added to the blend (Winterburn, 1994).

Several vendors have convinced Boeing customers that a 10 percent level of nylon will enhance the service life of the upholstery. There are probably no good data to prove the fact one way or the other; nylon does, however, enable vendors to operate looms at a faster rate, which affects price, as does the presence of the nylon.

FLAME-RETARDANT AND THERMALLY STABLE FIBERS

Boeing Materials Technology (BMT) considered six inherently flame-retardant or thermally stable fibers as candidates for airline application: CS Trevira (polyester), Nomex (aramid), P-84 (polyimide), PBI (polybenzimidazole), Kermel (polyamide-imide), and FR Viscose.

The rayon and polyester fibers contain FR additives that make them acceptable for airline usage, and both are readily available in a large palette of ultraviolet stable colors. Experience indicates that uses of FR Viscose within the airline industry is principally as a drapery material. While it was initially tried as an upholstery material, BMT found that the fiber cost was comparable to wool, the smoke numbers were equal or higher than wool, and the fiber did not have the abrasion resistance of the wool (Hasselbrack, 1980). The fiber producer tried altering the drawing of the molten polymer to increase the crystallinity or a scouring of the surface of the fiber to impart greater intra-yarn cohesiveness. A blend of wool and FR Viscose was tried, but there was no market niche for such a blend. At present, the greatest volume of FR Viscose is in the protective clothing market in blends with thermally stable polymers.

CS Trevira (FR polyester)

The Hoechst (Germany) CS Trevira fiber has penetrated the drapery and upholstery airline market in countries where dry cleaning facilities are nonexistent or very expensive. With the import tax into the United States, the fiber approximates the price of wool. The following details which must be considered when using Trevira upholstery: (a) only the texturized CS Trevira can be used because of the pilling propensity; (b) the finished fabric must be subjected to a carefully controlled singeing treatment to minimize pilling; (c) the fabric must either be run through the center frame in a relaxed state to minimize relaxation shrinkage, or be given a postloom scouring; and (d) CS Trevira has difficulty passing the Park Oil Burner test unless the fire blocker contains a high ratio of PBI. With PBI approximating a cost of $70 per pound, the fire blocker becomes costly and overshadows the savings realized by eliminating dry cleaning. However, two types of FR foams enable the CS Trevira to pass. While the airline industry is currently focused on CS Trevira, the U.S. division of Hoechst Celanese is beginning to pursue the airline market with their low-pill Trevira FR type 370, a staple yarn. The Trevira FR differs from the CS Trevira in two ways: (1) special additives in the monomer are designed to minimize the pilling problem; and (2) there is less of the FR additive in the U.S. polymer (O'Connor, 1994). As of this writing, the U.S. branch is just initiating work with the airline upholstery and drapery suppliers.

Nomex (aramid)

In the early days of the Boeing 747 (1968-1969), Nomex was used for carpeting and upholstery. These materials showed very poor color fastness in service and had to be replaced. However, two or three carriers continued to use Nomex carpet in three or four colors for about 10 years. Out of curiosity, a Nomex carpet was tested in the NBS smoke chamber for comparison with a BMS (Boeing Material Specification) qualified wool carpet. Observers were amazed at that time that the FR wool pile carpet with the appropriate backcoating produced less smoke than the Nomex pile carpet of comparable weight. With today's experience, the composition of the backcoating would be among the first questions asked. There is, however, little incentive to ask manufacturers to exert much effort to improve the smoke emission of a carpet: multiple investigations of crash incidents demonstrate that the carpet is almost never involved in the fire.

Since 1988, Nomex has been used as the standard rise/dado panel fiber, replacing wool, which initially could not pass the Low Heat Release Rule. At Boeing, our experience demonstrates that Nomex is a fiber plagued by serious dye-lot inconsistencies, a limited color palette, and ultraviolet instability. In addition to the greater cost per pound (about three times greater than wool), the CGF Nomex fiber requires solution dyeing, hence, a large minimum run. We find it difficult to obtain subsequent production lots with a color match close enough to enable placement of yardage from different production lots adjacent to each other. The color matching is done in the fiber state, so traditional instrumented color matching equipment is not entirely usable even though a common fiber-combing technique for color evaluation was worked out with DuPont. At present, color approvals of the dyed fiber are conducted under standard lighting conditions by the human eye. At times, the woven yardage made from the approved staple fiber "fluff" appears substantially off-shade, and a new fiber production run is required.

Furthermore, our customers complain about service "wear" issues and have filed warranties against Boeing. Two common complaints are (a) fiber splaying and fabric separation with minimum rubbing in the area where the fabric is folded over the top of the riser panel; and (b) a tendency toward some fabric raveling where it is rubbed by briefcases, shoe scuffing, or other abradants. DuPont is currently marketing an alternate Nomex fiber, Thermacolor. While there are no data to suggest that Thermacolor incorporates improved abrasion resistance, DuPont asserts that the fiber is feasible for risers and wall tapestries because (a) the fiber can be dyed at a commercial dye facility, thereby eliminating the cost of minimum runs; and (b) Boeing color approvals would be possible in the woven, tufted, or finished state. While there is no alternate fiber that can produce the white and light pastel colors desired for wall murals, the P-84 polyimide fiber, discussed next, has an ultraviolet stable color palette of over 50 colors.

P-84 (polyimide)

At the present time, the P-84 fiber is recommended for drapery and riser applications. It is available in multiple yarn sizes so it can be used in a wide variety of end uses, especially if blended with wool or cotton. Two drawbacks presently limit its usage: (1) it is a solution-dyed fiber with a minimum run of 250 pounds; and (2) it has poor abrasion resistance unless it is used in a blend. Except for research evaluations, the manufacturer (Lenzing) has not been asked to produce fiber for the airplane industry; but the fiber is widely used in the protective clothing industry in blends with Kevlar, PBI, and FR Viscose.

PBI (polybenzimidazole)

Because PBI can withstand the highest temperatures of all the thermally stable fibers before decomposing, it is an excellent fire blocker, especially as a needled felt in combination with difficult materials (e.g., leather upholstery). The PBI begins to break down when exposed to the light; the fiber is difficult to stabilize and shrinkage becomes a problem in garments; it does not have the strength of P-84; and the palette is limited to two or three harsh colors. There is a substantial cost differential between the two fibers: PBI costs approximately $70 a pound; P-84 costs about $22 a pound.

Kennel (polyamide-imide)

Kermel has not penetrated the airline textile market. An effort to stimulate interest among the fiber producers in Lyon in airplane applications led to the conclusion that the fiber does not have a unique application within the airplane. The fiber is costly to produce in small airplane quantities; and, to date, the color palette is limited to 14 solution-dyed colors. Kermel blended with FR Viscose is widely used in the protective clothing field because of the comfort due to good moisture absorption, and softness, and the fire protection provided even in a lightweight construction (7.5 oz/yd^2). A promotional brochure ("Kermel 7.5 oz. Argumentation: A Rhone Poulenc-Amoco Fibers Joint Venture") states that if Kermel is used in blends, it must be used with fibers that do not require dyes with "carriers" for the carriers have resulted in an unsafe garment condition due to fiber wicking.

SUMMARY AND CONCLUSIONS

I have tried to provide a comprehensive status overview of all the wool flame-retardant finishing technology used within the airline industry today, and the growing interest by the airline customer toward a washable product, which includes washable FR wool. A review of the advances that have improved fire safety within the passenger cabin over the past 15-20 years is an occasion for feeling a sense of pride and accomplishment. Boeing will continue our quest for materials that will enhance airplane fire safety. It is our belief that wool will remain the primary fiber for decorative applications because it possesses (1) an outstanding acceptance of dyestuffs; (2) inherent resistance to burning; (3) ease of flame retardance; and (4) a great capacity to tolerate the "wear and tear" of service life. It does not appear feasible that thermally stable fibers will become a significant entity within the passenger cabin because of their large minimum quantities, low abrasion, ultraviolet instability, color limitations, and high cost.

It remains to briefly address the controversial subject of nylon carpet. Each year more airlines elect to install nylon carpet because of the "throwaway" nature of airline carpeting. The entryway and aisles have to be replaced within 3 or 4 weeks, in spite of attempts at good maintenance. Nylon's low cost, coupled with a longer wear life in a lightweight construction, cannot be matched in wool. Because nylon fiber itself is not manufactured as an inherently flame-retardant polymer, a PVC compound must be placed in the backcoating to enable the carpet to pass the 12-second vertical Bunsen burner test. Insofar as accident investigations demonstrate that the carpet is rarely involved in the fire, there is no need for great concern about the quantities of smoke produced in the smoke chamber when comparing nylon to wool carpets. It would be more realistic to change the flammability test for carpet to a horizontal position, for that orientation represents its actual use; also, the high smoke producing backcoating could be replaced with the types of backcoating used on wool carpets—vinyl acetate/ethylene copolymer or styrene butadiene with alumina trihydrate as the filler for both compounds (Benisek and Phillips, 1977a).

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Smoke Toxicity*

*David Purser***

SUMMARY

When aircraft cabin occupants are exposed to fire effluent the first hazard encountered is usually smoke, containing particulates and toxic gases that cause immediate visual obscuration and painful irritation of the eyes and respiratory tract. This may be followed by incapacitation due to pain or asphyxia if exposure continues. In smouldering or small, confined, in-flight fires, where the yields of organic irritants and acid gases are likely to be high and exposure times long, the distressing effects of irritants, lung inflammation, and asphyxia induced by carbon monoxide are likely to be the main hazards. For post-crash fires, which tend to develop rapidly to flashover, the time available for escape is often limited to a few minutes before conditions become lethal due to the effects of toxic smoke and heat, so that survival depends upon a rapid egress. Visual obscuration and smoke irritancy are important during the early stages in that they may reduce the speed and efficiency of escape. People have been shown to be reluctant to enter smoke-logged areas if these are between them and an exit, and movement speeds are greatly reduced at optical densities above 0.5, OD/m and even more when the smoke is irritant. Once cabin lining and seating materials become heavily involved in the area opposite a cabin breach, then the concentrations of toxic gases, especially carbon monoxide (CO) and hydrogen cyanide (HCN), can increase rapidly further down the cabin, causing rapid incapacitation of any remaining cabin occupants. This is followed or accompanied by extreme heat, so that deaths result from asphyxia and/or heat shock. For in-flight fires, it is recommended that consideration should be given to reducing the hazard from irritants. For post-crash fires, measures aimed at delaying the involvement of cabin contents (such as spray mist systems) should be considered.

INTRODUCTION

The majority of fatal and nonfatal casualties from fires result from exposure to toxic smoke, but there can be considerable differences between different types of fires in terms of the smoke composition and the ways in which it affects people in different fire scenarios. Fires in aircraft may be classified into two very different major categories, the in-flight fire and the post-crash fire.

Aircraft occupants in flight may be many hours from possible landing and disembarkation, so that any fire that grows rapidly and penetrates the cabin space is likely to be fatal, due to asphyxiation of the occupants and loss of the aircraft. Fortunately such occurrences are rare, but of equal concern must be the small nonflaming or flaming fire, particularly in a

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confined space. This may result in contamination of the cabin atmosphere with a low concentration of toxic smoke that may have to be endured for a number of hours. In such situations the major concerns must be initially the psychological and physiological effects on passengers and crew of exposure to an irritant and optically obscure smoke, and then the asphyxiation hazards presented by lung inflammation and gradual intoxication by asphyxiant gases such as carbon monoxide, both of which may lead to long-term respiratory tract and neural damage in survivors.

Post-crash fire scenarios are very different because they often involve large, rapidly growing fires resulting from fuel involvement, which may enter the cabin through breaches and result in rapid cabin flashover. Also, because the aircraft is on the ground, rapid passenger egress or rescue may be possible. In this situation the key factors are the time within which the passengers can disembark compared with the rate of fire growth and particularly the time within which toxic smoke and heat impair or prevent egress.

This paper examines fire scenarios in terms of toxic smoke and heat profiles and presents methods for estimating behavioral impairment and incapacitation.

PRACTICAL METHODS FOR THE ASSESSMENT OF FACTORS DETERMINING HAZARD TO LIFE IN FIRES

From the point of view of parameters directly related to the fire process, the development of behavioral impairment and hazard to life depends upon two major parameters:

1. The time-concentration (or intensity) curves for the major toxic products, optically dense smoke, and heat in the fire at the breathing zone of the occupants, which in turn depend upon:
    - the fire-growth curve in terms of the mass-loss rate of the fuel (kg/s) and the volume into which it is dispersed (kg/m^3); and
    - the yield of toxic-products smoke and heat in the fire (e.g., kgCO/kg of material burned).
2. The toxic potency of the products (the exposure concentration [kg/m^3], or exposure dose [kg min/m^3 or ppm min] required to cause toxic effects (and the equivalent effects of heat and smoke obscuration), the assessment of which requires consideration of three aspects:
    - exposure concentrations or doses likely to impair or reduce the efficiency of egress due to psychological and/or physiological effects;
    - exposure concentrations or doses likely to produce incapacitation or prevent egress due to psychological and/or physiological effects; and
    - lethal exposure concentrations or doses.

There are essentially two practical methods assessing these factors:

1. from large-scale fire tests including measurements of the concentration-time profiles of the major toxic gases, heat, and smoke optical density, and from existing knowledge of the effects of exposure to these agents; and
2. from a battery of small-scale tests and mathematical models, or simple large-scale tests, where the essential elements are:

   - the toxic potency data for the materials (lethal mass-loss exposure dose [gm · min/m^3]) obtained from small-scale tests; and
   - the mass-loss/concentration curve for the fire.

From the point of view of understanding effects on people in fires, full-scale fire tests are the most valuable, since they enable the concentration-time profiles of the heat and toxic smoke to be measured directly at different levels and positions within the fire. In practice, however, elements of both methods are useful in making an overall assessment. The second method is used mainly for evaluating materials with regard to the lethal toxic potency of potential fire atmospheres. In order to enable the effects of exposure of people to fire hazards to be calculated, a series of algorithms has been developed for calculating time to incapacitation or death, which is published in The SFPE Handbook of Fire Protection Engineering (Purser, 1988), in a NATO-AGARD (Advisory Group for Aerospace Research and Development) paper on aircraft fires (Purser, 1989), and in BSI (British Standards Institution) and ISO (International Standards Organization) technical reports (BSI, 1989; ISO, 1994).

Physiological Hazards in Fires

The physiological effects of exposure to toxic smoke and heat in fires result in varying degrees of incapacitation, which may also lead to death or permanent injury (Purser, 1988). Incapacitating effects include:

a. Impaired vision resulting from the optical opacity of smoke and from the painful effects of irritant smoke products and heat on the eyes.
b. Respiratory tract pain and breathing difficulties or even respiratory tract injury resulting from the inhalation of irritant smoke, which may be very hot. In extreme cases this can lead to collapse within a few minutes from asphyxia due to laryngeal spasm and/or bronchoconstriction. Lung inflammation may also occur, usually after some hours, which can also lead to varying degrees of respiratory distress.
c. Narcosis from the inhalation of toxic gases, resulting in confusion and loss of consciousness.
d. Pain to exposed skin and the upper respiratory tract followed by burns, or hyperthermia, due to the effects of heat, preventing escape and leading to collapse.

All of these effects can lead to permanent injury, and all except (a) can be fatal if the degree of exposure is sufficient.

With regard to hazard assessment the major considerations are:

1. the time when partially incapacitating effects that might delay escape are likely to occur;
2. the time when incapacitating effects that might prevent escape are likely to occur, compared with the time required for escape; and
3. whether exposure is likely to result in permanent injury or death.

Up to a certain level of severity, the hazards listed in (a)-(d) above cause a partial incapacitation by reducing the efficiency and speed of escape. These effects lie on a continuum from little or no effect at low levels to relatively severe incapacitation at high levels, with a variable response from different individuals. It is important to make some estimate of effects that are likely to delay escape; these effects may decrease the number of occupants able to escape during the short time before conditions become so bad that escape is no longer possible. Most important in this context is exposure to optically dense and irritant smoke, which tends to be the first hazard confronting fire victims. For more severe exposures, a point may be reached where incapacitation will prevent escape. For some forms of incapacitation, such as the point where narcosis leads to a rapid change from near normality through a brief period of intoxication, to loss of consciousness, this point is relatively easy to define. For other effects an endpoint is less easily defined; examples are the point where smoke becomes so irritant that pain and breathing difficulties lead to the cessation of effective escape attempts, or the point where pain and burns prevent movement. Nevertheless it is considered important to attempt some estimate of the point where conditions become so severe in terms of these hazards that effective escape attempts are likely to cease, and where occupants are likely to suffer severe incapacitation or injuries.

In addition to the physiological effects of exposure to toxic smoke, there are psychological factors to be considered in relation to smoke exposure. This aspect is largely beyond the scope of this paper but some aspects are mentioned in the next section.

Evaluation of the Effects of Optically Dense, Irritant Smoke on the Eyes and Respiratory Tract

Optically dense smoke affects way-finding ability and the speed of movement of occupants, and a smoke barrier may be perceived as being impenetrable. These effects depend upon the concentration (optical density) of the smoke and its irritancy to the eyes and respiratory tract. In experiments where people were asked to walk down a smoke-logged corridor, Jin (1976) found that for nonirritant smoke, walking speed decreased with smoke density, and that at an optical density of 0.5 OD/m (extinction coefficient 1.15) walking speed decreased from approximately 1.2 m/s (no smoke) to 0.3 m/s. Under these conditions people behaved as if they were in total darkness, feeling their way along the walls. When people were exposed to irritant smoke, made by heating wood chippings, movement speed was reduced to that in darkness at a much lower optical density (0.2 OD/m, extinction coefficient 0.5), and the experience was found to be more distressing.

In addition to these effects upon movement speed, there is the problem of deciding whether people will move at all. In a number of studies of fires in buildings, a proportion of people (approximately 30 percent) were found to turn back rather than continue through smokelogged areas (Wood, 1972; Bryan, 1977). The average density at which people turned back was at a "visibility" distance of 3 m (0.33 OD/m), and women were more likely to turn back than men. A difficulty with this kind of statistic is that in many fires in buildings there is a choice between passing through smoke to an exit or turning back to take refuge in a place of relative safety, such as a closed room. In some situations people have moved through very dense smoke when the fire was behind them, while in other cases people have failed to move at all. In a post-crash (or grounded) aircraft fire it seems likely that the majority of people will attempt to move through even dense smoke towards an exit, especially if layering permits them to crouch down to levels where the smoke density is lower and if low-level lighting is used to improve visibility. However, it is likely that some people will not move through dense smoke.

Smoke irritants consist of inorganic acid gases (such as hydrogen chloride) and organic compounds, particularly low molecular weight aldehydes (formaldehyde and acrolein). More than 20 irritant substances have been detected in smoke, and it is considered that others remain to be identified (Purser, 1988). The first effect of exposure to smoke irritants is sensory irritation, which consists of painful stimulation of the eyes, nose, throat, and lungs. Sensory irritation depends upon the immediate concentration of irritants to which the subject is exposed rather than a dose acquired over a period of time, the effects lying on a continuum from mild eye irritation to severe eye and respiratory tract pain. In evaluating this aspect of irritancy the aim is to predict what concentration of mixed irritant products is likely to cause such pain and difficulty in breathing that escape attempts would be slowed or rendered less efficient, and what concentration is likely to seriously disrupt or prevent escape (a degree of incapacitation approximately equivalent to that at the point of collapse resulting from exposure to narcotic gases). For example, with regard to hydrogen chloride it is considered that concentrations of approximately 100-500 ppm would be painfully irritant, and that the effects might slow escape but probably not prevent it. However, at approximately 1,000 ppm and above it is suggested that the effects might be so severe as to prevent escape (Purser, 1988, 1989). In the absence of detailed information on irritant mixtures it is assumed that all irritants would be additive in their effects, since they are all capable of causing damage to lung tissue. In large-scale fire tests it is possible to measure inorganic irritants directly, but it is difficult to assess the degree of irritancy from organic products, which form a very important component. In general the effects of organic irritants depend on the concentration of partially oxidised organic species in the smoke. For example, smokes from smouldering wood or polyolefins have a high organic content and are highly irritant; they are characterised by low CO_2/CO ratios and high smoke yields. Under well-ventilated flaming conditions, by contrast, the organic content of the effluents is low and irritancy is low. In general, it is predicted that smoke from a mixed fuel source with an optical density/meter of 0.5 would be strongly irritant to the eyes and respiratory tract (Jin, 1976; Purser, 1988). However, for a given smoke density there are differences between different types of fires, since some people report that smoke from some fires, while dense optically, is relatively low in irritancy, while that from other fires is extremely irritant.

It is difficult to quantify these irritant effects because the database on the effects of individual irritants or irritant mixtures on escape behavior in humans is poor and because the effects lie on a continuum of severity where there are no precise endpoints. Assessment has to be based upon a small number of human experimental exposures (usually at relatively low concentrations), accidental exposures, and the results of bioassay studies. The most useful bioassay method for sensory irritation has been the mouse RD_{50} test, in which the concentration causing a 50 percent decrease in respiration rate following a short exposure is measured. A reasonably good relationship has been found between the mouse RD_{50} concentrations for a range of irritant vapours and the concentrations reported as being painfully irritant to humans (Alarie, 1981). The test has been applied to a wide range of irritant substances, many of which occur in fire atmospheres, and also to mixed combustion product atmospheres.

In order to assess the combined effects of irritants, a concept of fractional irritant concentration (FIC) has been developed (Purser, 1993), whereby the concentration of each irritant present is expressed as a fraction of the concentration considered to be severely irritant to humans. The irritant concentration for each gas has been set on the basis of data from both human and animal studies. The FICs for each irritant are then summed to give a total FIC. If the total FIC reaches unity, then it is predicted that the smoke atmosphere would be highly irritant, sufficient to slow down escape attempts. If the total greatly exceeds unity then it is likely that escape would be prevented, and it is possible that collapse might occur due to static hypoxia from bronchoconstriction or laryngeal spasm. On the basis of available data, current estimates of the concentrations of each gas likely to be highly irritant are as follows:

Toxic gas	Concentration
HCl	200 ppm
HBr	200 ppm
HF	120 ppm
SO_2	30 ppm
NO_2	80 ppm (5 min) 25 ppm (30 min)
Total organics	0.5 OD/m

On the basis of the assumption that all irritants capable of damaging lung tissue are additive in their effects, the overall irritant concentration FICirr is then given by

$$FIC_{irr} = FIC_{HCl} + FIC_{HBr} + FIC_{HF} + FIC_{SO2} + FIC_{NO2} + FIC_{org} \; . \qquad (1)$$

Another way of expressing the sensory irritancy of fire effluent is in terms of the RD50 of the material decomposed (expressed as the mass-loss concentration), rather than in terms of individual irritant products. Table 1 shows the mouse RD_{50} for a number of materials, some of which are used in aircraft, when decomposed under the thermal decomposition conditions indicated, using the FRS tube furnace method (Purser et al., 1994). The majority of experiments were conducted under nonflaming oxidative decomposition conditions, but a small number of experiments were conducted under flaming decomposition conditions. The results show that the majority of materials have RD$_{50}$values lying between 0.05 and 0.5 g/m^3 under nonflaming oxidative decomposition conditions. This means that if the products of decomposition of between 0.05 and 0.5 grams of material are dispersed into each cubic metre of air, then the resultant atmosphere is predicted to be painfully irritant to the eyes and respiratory tract. However, under flaming decomposition conditions the smoke irritancy decreases by a factor of 10 or more. The other important effect of irritants is that a proportion of those inhaled penetrate into the deep

TABLE 1 Mass-Loss Concentration of Thermal Decomposition Products Predicted to be Painfully Irritant (mouse RD50 g/m3)

Material	Temperature (°C)	NF/F[a]	RD$_{50}$ g/m^3	95% Confidence Limits
General Materials				
Acrylonitrile butadiene styrene	500	NF	0.11	0.07-0.17
Acrylonitrile butadiene styrene	600	F	~**1**	
Low density polyethylene	500	NF	0.05	0.03-0.07
Nylon-6	480	NF	0.47	0.29-1.10
Nylon-6	600	F	-20	
Polyvinylchloride (PVC) (rigid)	400	NF	0.17	0.12-0.25
PVC (plasticised)	380	NF	0.19	0.09-0.28
PVC (plasticised)	600	NF	0.17	0.12-0.22
PVC (plasticised)	650	F	-2.6	
Thermoplastic polyurethane	425	NF	0.20	0.14-0.96
Thermoplastic polyurethane	600	F	~3	
Cable Materials				
PVC insulation (plasticised)	550	NF	0.56	0.39-1.00
PVC jacket (plasticised)	550	NF	0.34	0.27-0.47
Cross-linked polyethylene (insulation)	550	NF	0.12	0.09-0.17
Cross-linked polyethylene (jacket)	550	NF	0.32	0.20-0.32
Aircraft Materials				
Phenolic fiberglass	600	NF	>9.1	
PVC decorative laminate	600	NF	0.10	
Polycarbonate	600	NF	0.25	
Phenolic oil fiberglass insulation	600	NF	0.05	
Aluminised PVF/paper covering	600	NF	0.37	
Redux adhesive	600	NF	0.10	0.06-0.16
Silicone rubber	600	NF	0.06	0.01-0.29
Joining compound JC5V	600	NF	0.18	0.07-0.32
Viton sealant	600	NF	0.21	0.15-0.27
Berger elastomer	600	NF	1.38	1.12-1.80

[a] NF = nonflaming, F = flaming.

lung. If a sufficient dose is inhaled over a period of time a lung inflammatory response can occur, usually some hours after exposure. This may cause respiratory failure and death, or permanent lung damage in survivors. The 30-minute exposure concentrations likely to be lethal used for each irritant gas (based upon rat LC_{50} data) are as follows:

Toxic gas	Concentration
HCl	3,800 ppm
HBr	3,800 ppm
HF	2,900 ppm
SO_2	400 ppm
NO_2	170 ppm (30 min), 375 ppm (5 min)
Total organics	3 OD/m

The effects depend upon the exposure dose, which can be quantified approximately in terms of the product of concentration (c) and exposure time *(t)* to give the *ct* product exposure dose (ppm/min). During a fire, when the concentrations of the toxic products vary with time, it is possible to predict when an incapacitating or lethal dose has been received by using the fractional effective dose (FED) method. For this method the *ct* product doses for small periods of time during the fire are expressed as a fraction of the dose causing a toxic effect, and these FEDs are summed until the fraction reaches unity, when the toxic effect is predicted. The fraction of a lethal dose (FLD) for each irritant is calculated as the *ct* product exposure dose during a period in the fire (e.g., in ppm/min) expressed as a fraction of the lethal exposure dose. The lethal effects of the different irritants are assumed to be additive on the same basis as the irritant effects, so that the total FLD_{irr} for each time period is given by

$$\mathrm{FLD}_{irr} = \mathrm{FLD}_{HCl} + \mathrm{FLD}_{HBr} + \mathrm{FLD}_{HF} + \mathrm{FLD}_{SO2} + \mathrm{FLD}_{NO2} + \mathrm{FLD}_{org}\ . \qquad (2)$$

Calculation of Time to Incapacitation Due to Effects of Narcotic Gases

Narcotic gases (carbon monoxide, hydrogen cyanide, carbon dioxide, and reduced oxygen) affect the nervous and cardiovascular systems, causing confusion followed by loss of consciousness, followed ultimately by death from asphyxiation (Purser, 1988). As narcotic gases are inhaled during a fire, an increasing dose builds up in the body. There is little effect initially, but when a critical threshold dose level is reached severe effects occur suddenly. These consist of a brief period of intoxication (similar to severe alcohol intoxication), followed by a collapse into unconsciousness (Purser, 1988). Where several narcotic gases are present the effects have been found to be additive, with carbon dioxide mainly causing an increase in the rate of uptake of the other narcotic gases. It has also been shown that the effects of irritant gases such as hydrogen chloride (HCl) are additive with those of carbon monoxide (Hartzell et al., 1985).

Based upon these findings, an FED equation to predict time to incapacitation (loss of consciousness from the effects of narcotic gases for humans) has been developed as follows:

$$FED_{IN} = (FED_{Ico} + FED_{Icn} + FED_{irr}) \text{ x } VCO_2 + FED_{Io} \text{ or } F_{Ico2} \text{ ,} \qquad (3)$$

where

FED_{IN} = fraction of an incapacitating dose of all narcotic gases;

FED_{Ico} = fraction of an incapacitating dose of CO;

FED_{Icn} = fraction of an incapacitating dose of HCN;

FED_{irr} = fraction of an irritant dose contributing to hypoxia;

VCO_2 = multiplication factor for CO_2-induced hyperventilation;

FED_{Io} = fraction of an incapacitating dose of low oxygen hypoxia; and

FED_{Ico2} = fraction of an incapacitating dose of CO_2.

Each individual term in the FED equation is itself the result of the following equations, which give the FED for incapacitation for each gas and the multiplication factor for CO_2, where *t* is the exposure time at a particular concentration in minutes. The FEDs acquired over each period of time during the fire are summed until the total FEDIN reaches unity, at which point incapacitation (loss of consciousness) is predicted. Death is predicted at approximately 2-3 times the incapacitating dose.

$$FED_{Ico} = (8.2925 \cdot 10^{-4} \cdot \text{ppm } CO^{1.036}) \cdot t/30 \text{ ,} \qquad (4)$$

$$FED_{Icn} = t/[\exp(5.396 \cdot 0.023 \cdot \text{ppm HCN})] \text{ ,} \qquad (5)$$

$$FED_{Irr} = \text{calculated in Equation 2 above ,}$$

$$VCO_2 = \exp(0.1903 \cdot \%CO_2 + 2.0004)/7.1 \text{ ,} \qquad (6)$$

$$FED_{Io} = t/\exp[8.13 - 0.54(20.9 - \%O_2)] \text{ , and} \qquad (7)$$

$$FED_{Ico2} = t/\exp(6.1623 - 0.5189 \cdot \%CO_2) \text{ .} \qquad (8)$$

Table 2 shows a simplified lookup table of FEDs for incapacitation for each gas for use in approximate calculations.

TABLE 2 Simplified Lookup Table for Solutions to Individual Toxic Gas FED Equations

FED_{Ico} = CO ppm/25,000

ppm HCN	FED_{Icn}	$\%CO_2$	VCO_2	$\%O_2$	FED_{IO2}	$\%CO_2$	FED_{Ico2}
0-5	0	0-2	1.0	21-13	0	0-2	0.01
50-100	0.05	2-3	1.5	13-12	0.02	2-3	0.01
100-125	0.10	3-4	2.0	12-11	0.05	3-4	0.02
125-150	0.15	4-5	2.5	11-10	0.08	4-5	0.03
150-200	0.50	5-6	3.0	10-9	0.15	5-6	0.05
200+	0.100	6-7	3.5	9-8	0.20	6-7	0.08
		7-8	4.5	8-7	0.40	7-8	0.13
		8-10	4.8	7-6	0.70	8-9	0.22
						9-10	0.38

Calculation of Time to Incapacitation Due to the Effects of Convected and Radiant Heat

Another dose-related hazard is exposure to convected heat, where skin pain followed by burns or hyperthermia occurs depending upon the air temperature and exposure time. A FED equation for heat has been developed similar to that for a narcotic gas, as follows:

$$FED_{Ih} = 1/\exp(5.1849 - 0.0273 \bullet \text{temp } ^\circ\text{C}) .$$

(9)

For radiant heat, skin pain and burns occur rapidly at intensities above 0.25 W/cm² (Purser, 1988). Details of the calculation methods are given in Purser, 1988 and 1989.

APPLICATION OF THE INCAPACITATION MODEL TO DIFFERENT FIRE SCENARIOS

In terms of the basic scenarios, the hazards in terms of the yields of heat, smoke, and toxic products, and the effects on escape behavior, fires can be considered in several different categories. The main categories are

1. nonflaming or smouldering fires where the victim is in the compartment of fire origin or in a remote location;
2. early-flaming, well-ventilated fires where the victim is in the compartment of fire origin or in a remote location;
3. small, restricted-ventilation fires where the victim is in the compartment of fire origin; and

4. ventilation-controlled post-flashover fires with low and high ventilation, where the victim is remote from the fire, either inside a very large compartment or outside the fire compartment.

In the context of aircraft fires, the first three categories are of concern mainly in the in-flight situation, where cabin occupants and crew may be exposed to fire effluent for several hours. Although fires in categories 2 and 3 may also present a hazard on the ground, it is to be expected that the aircraft would be cleared before such fires become a serious threat. The main hazard on the ground is therefore from fires, usually involving fuel, that rapidly grow very large and cause rapid flashover inside the cabin.

Nonflaming or Smouldering Fires

Nonflaming or smouldering decomposition results in high yields of organic irritants from materials, and high yields of inorganic irritants from materials containing the appropriate elements. These smoke irritants are predicted to cause distress upon initial exposure, due to the painful effects upon the eyes and lungs. As Table 1 shows, very small amounts of material can produce severely irritant atmospheres if decomposed under these conditions. Cases have occurred where the decomposition of a few tens of grams of cable insulation material have rendered large buildings uninhabitable for a number of hours. Prolonged exposure to these irritants over periods of an hour or more may lead to lung inflammation, while carbon monoxide intoxication may also occur.

A number of deaths each year result from fires in buildings that are considered to have undergone a prolonged period of smouldering. This may occur in items of furniture, or in structural items such as flooring, or in concealed cavities, sometimes initially involving smouldering cables. A recent case involving a number of deaths resulted from smouldering floorboards and joists. Nonflaming decomposition is slow, so that a relatively long time (approximately an hour or more) is required for the development of hazardous conditions. However, although small masses of material may be decomposed, the yields of carbon monoxide can be high, and these conditions generally provide the highest yields of irritant organic products. The major hazard is to a sleeping or otherwise incapacitated occupant of a closed room, or to aircraft occupants in flight who may be overcome by carbon monoxide and lung damaging irritant smoke.

A good example of such a situation is presented by a series of tests carried out at the National Institute of Standards and Technology (Braun et al., 1987; Purser, 1990) where two types of armchair made from a standard and a fire-retarded (FR) polyurethane foam with cotton covers (combustible mass 5.7 kg) (see Tables 3 and 4) were burned in a simulated small apartment (volume 101 m^3) consisting of a burn room (11.8 m^3) connected via a corridor 12 m long to a target room (volume 12.08 m^3). The chairs were tested by flaming ignition of the seat back, and also by smouldering caused by one or two cigarettes placed in the seat angle for approximately 1 hour, followed either by spontaneous flaming or ignition from a flaming source. Under smouldering conditions, approximately 1 kg of foam was decomposed in just over 1 hour.

TABLE 3 Concentrations of Toxic Gases and FEDs in Burn Room for Smouldering Followed by Flaming Ignition of Standard Foam Armchairs versus Time (in minutes)

	0-13	13-27	27-40	40-53	53-67	67-75	75-76
Gas Concentrations							
CO (ppm)	180	300	360	700	700	1,000	10,000
HCN (ppm)	0	0	0	0	0	0	1,320
CO$_2$ (%)	0.11	0.16	0.18	0.30	0.30	0.40	15.0
O$_2$ (%)	21	21	21	21	21	21	3
FEDs for Incapacitation							
FED$_{co}$	0.006	0.010	0.012	0.024	0.24	0.024	Immediately fatal
FED$_{HCN}$	0	0	0	0	0	0	
VCO$_2$	1.019	1.032	1.037	1.069	1.069	1.096	
FED$_o$	0	0		0	0	0	
FED/min	0.006	0.010	0.013	0.026	0.026	0.039	
Σ FED	0.078	0.218	0.387	0.725	1.089[a]	1.401	

[a] By 71 minutes the mass-loss exposure dose of irritants was 600 g·m-^{3}·min, which is likely to cause fatal lung damage.

TABLE 4 Concentrations of Toxic Gases and FEDs in Target Room for Smouldering Followed by Flaming Ignition of Standard Foam Armchairs versus Time (in minutes)

	0-13	13-27	27-40	40-53	53-67	67-75	75-76	76-77
Gas Concentrations								
CO ppm	0	0	100	270	550	800	2,700	2,000
HCN ppm	0	0	0	0	0	0	125	120
CO$_2$ %	0.04	0.04	0.08	0.15	0.20	0.30	9.00	8.50
O$_2$ %	21	21	21	21	21	21	13	14
Doses of Incapacitation								
		FED$_{co}$	0.003	0.009	0.019	0.028	0.099	0.073
FED$_{HCN}$			0		0	0	0.080	0.072
VCO$_2$			0.012	1.030	1.042	1.069	5.772	5.248
FED$_o$			0		0	0	0.021	0.012
FED/min	0	0	0.003	0.009	0.020	0.030	1.054	0.773
Σ FED	0	0	0.039	0.156	0.436	0.676	1.730[a]	2.503

[a] By 71 minutes the mass-loss exposure dose of irritants was approximately 300 g·m-3·min, which may cause some lung damage.

The smoke layer had reached the floor after an hour, but there was a concentration gradient for smoke and toxic gases between the burn room and the target room. The major narcotic gas present was CO, which gradually increased in concentration in the burn room from 180 ppm during the first 13 minutes to 1,000 ppm at 67-75 minutes. This was sufficient to have caused incapacitation (loss of consciousness) in just over 1 hour in the burn room but probably not in the target room, where the concentration was lower. When flaming ignition occurred, the chair burned very rapidly and produced high concentrations of narcotic gases, which would have been almost immediately fatal in the burn room. Within the target room an occupant would have become unconscious within less than 1 minute and received a fatal dose within 2 minutes. The smoke in the system was also very irritant, and it is likely that anyone spending more than 1 hour in the burn room would have suffered serious and possibly fatal lung damage, even if they had been rescued. This example illustrates the dangers of smouldering, which can continue for several hours and spread lethal products throughout a building. It is therefore dangerous to a sleeping, trapped, or otherwise incapacitated occupant. Since such fires often change to flaming before they are discovered, it is difficult to know the true incidence of incapacitation and death occurring during the nonflaming phase of fires. For this example both the standard and FR chairs would have caused incapacitation after 1 hour in the burn room, but due to its higher yield of CO and irritants, the FR chair would also cause incapacitation in the target room soon after, and death in the burn room after 1.5 hours of smouldering. For the standard foam, death at both locations would occur within 1 minute of the spontaneous transition to flaming after 75 minutes.

Early-Flaming, Well-Ventilated Fires in a Room with an Open Doorway

In early-flaming fires, the decomposition conditions, particularly the air/fuel ratio, and the type of fuel are major determinants of the yields of toxic gases. In early-flaming, well-ventilated fires involving non-fire-retarded materials, combustion is usually efficient, so that the main products are heat, carbon dioxide, and water, the yields of toxic products and smoke being relatively low. However, when inefficiently burning materials are present, or when the fire grows to a large size relative to that of the compartment, so that the ventilation may become restricted even with an open doorway, then toxic products may become important as well as heat. The example shown in Table 5 gives the results obtained during the first 5 minutes of a burn with flaming ignition of a rather bad single armchair (polystyrene with polyurethane cushions and covers) in a room with an open doorway. For an occupant of the room during the fire the following effects are predicted:

1. Towards the end of the second minute and the beginning of the third minute, the smoke optical density and mass loss would sufficiently exceed the escape limitation thresholds for visual obscuration and sensory irritation to severely inhibit escape from the room.
2. During the fourth minute, the average temperature is 220 °C, and sufficient heat would be accumulated in the skin surface to cause skin burns resulting in incapacitation.

TABLE 5 FED Analysis of Toxic and Physical Hazards from a Chair Burning in an Open Room

	1 min	2 min	3 min	4 min	5 min
Average Gas Concentrations					
CO (ppm)	0	0	500	2,000	3,500
HCN (ppm)	0	0	0	75	125
CO_2 (%)	0	0	1.5	3.5	6
O_2 (%)	20.9	20.9	19	17.5	*15*
Fractional Incapacitating Doses					
FED_{co}	0.00	0.00	0.017	0.074	0.130
FED_{HCN}	0.00	0.00	0.000	0.025	0.080
VCO_2	1.00	1.00	1.442	2.376	4.434
$FEDO_2$	0.00	0.00	0.001	0.002	0.007
FED/min	0.00	0.00	0.026	0.235	0.938
Σ FED	0.00	0.00	0.026	0.261	1.199
Doses of Convected Heat					
Temp °C	20	65	125	220	405
FED/min	0	0.033	0.170	2.273	355
Σ FED	0	0.033	0.203	2.476	355
	Radiant Heat Flux				
W/cm²	0	0.01	0.04	0.10	0.25

3. During the fifth minute, a victim is likely to lose consciousness due to the combined effects of the accumulated doses of narcotic gases. The threshold limit for pain from radiant heat is also reached.
4. An occupant escaping or rescued after the fourth minute would suffer severe post-exposure effects due to skin burns, possible laryngeal burns with accompanying oedema and danger of obstructive asphyxia, and also lung oedema and inflammation which might well be fatal (due to the combined effects of inhaled hot gases, chemical irritants, and the pulmonary secondary effects of skin burns). After the sixth minute, it is likely that a victim would die at some time between a few minutes and 1 hour due to the effects of narcosis, circulatory shock, and possibly hyperthermia.

In an aircraft in flight, a growing flaming fire is obviously a very serious hazard, and is likely to cause incapacitation within minutes unless it is contained within an unoccupied, closed compartment or rapidly extinguished. Fires within small, concealed spaces are likely to be subject to restricted ventilation, which results in additional hazards, as described in the next section. For flaming fires on the ground, the main consideration is the fire-growth rate and the time required for the occupants to disembark. Although aircraft materials have a high standard of fire resistance, it is possible to conceive of a number of situations in which rapid fire growth could occur.

With regard to people's perception of the smoke from these and other fires, there seems to be a considerable variation in the effects, depending upon what is burning. For example, in a recent fire a cotton-covered coconut-matting sofa burned in an open room in a two-story apartment. The apartment and the corridor outside it became logged with a thick smoke, but a number of persons were able to move through the smoke without difficulty (although the occupants perceived the smoke to be too dangerous to escape through and retreated to a bedroom, from which they were rescued). In some situations it is possible to account for effects on fire victims in terms of the classical toxicology models described, but in others the smoke appears to be much worse than would be predicted. For example, a fire fighter reported that he inhaled a whiff of smoke from the burning interior of a car and immediately almost fainted. In some major fire disasters, such as the Woolworth fire in Manchester (England) in May 1979 and the Dupont Plaza Hotel fire, victims have been found dead, sitting at tables with food, in the latter case only a few feet from a safe exit. Such individuals have apparently been overcome by smoke inhalation so quickly that they have been unable to move, possibly by a single breath of smoke. It would seem that this would be most likely to occur to a victim remote from the site of a pre- or post-flashover fire that has become vitiated, who is suddenly exposed to smoke containing a very low oxygen concentration and very high concentrations of toxic effluents.

Small, Restricted-Ventilation Fires in Closed Compartments

Another very hazardous situation is that of a fire in a closed room. In this situation a smouldering or especially a flaming fire quickly uses up the available oxygen, and as the oxygen concentration falls after a minute or so the combustion becomes inefficient, producing a dense smoke rich in carbon monoxide and other toxic products. These, together with the lowered oxygen concentration in a room, can produce a rapidly lethal atmosphere. An example is a recent fire involving an adult and a 4-year-old child. Both were in a small bedroom for a short time during which the adult went to sleep and the child is thought to have ignited a small piece of foam using a cigarette lighter. The fire was discovered after a few minutes, when the door was opened by a family member, who extinguished the very small fire with a bucket of water. Both the adult and child were dead, with blood carboxyhaemoglobin concentrations of about half a lethal level. Based upon the dimensions of the room, it is calculated that the decomposition of approximately 0.5 kg of material would be sufficient to lower the oxygen concentration towards 10 percent and give carbon monoxide concentrations of approximately 1 percent or more, which together with other toxic products would cause incapacitation and death within a few minutes. In an aircraft in flight, a small, poorly ventilated, flaming fire could therefore present a serious hazard from the high yields of carbon monoxide and hydrogen cyanide and the consumption of oxygen.

Fully Developed/Post-Flashover Fires

The final situation to consider is that where the occupants are remote from the site of a large fire, either in a large compartment or at a location remote from the fire compartment. This is the situation leading to the major multiple-death disasters, and against which most regulatory requirements for passive and active fire protection are designed to provide protection. Once a fire has reached a large size, the rate of burning and of the evolution of heat and toxic smoke is very great, so that even a large building can be rapidly filled with smoke. The decomposition conditions in such fires depend upon the ventilation, but most fully developed fires in buildings tend to be hot and oxygen vitiated. These conditions favour inefficient combustion, with high yields of dense smoke containing high concentrations of carbon monoxide, hydrogen cyanide, and low oxygen. An example of such a fire is the penetration of a large external fuel fire into the cabin of an aircraft, as happened in the Manchester Airtours fire (King, 1989). Table 6 shows the results obtained inside the cabin of a Boeing 707 containing a few rows of seats opposite an open doorway, outside which were 200 litres (50 U.S. gallons) of burning aviation fuel (Avtur) (Fardell and Purser, 1991). The rapid involvement of the cabin contents gave rise to a dense smoke containing large amounts of carbon monoxide and hydrogen cyanide at a measurement point halfway down the fuselage. It is predicted that escape capability is likely to be severely inhibited after approximately 1-1.5 minutes due to the effects of exposure to the dense smoke containing high concentrations of acid gases and organic irritants. Severe incapacitation (loss of consciousness) is predicted after just 2 minutes, followed rapidly by death, mainly from the effects of hydrogen cyanide (high concentrations of which were found in the blood of the Manchester victims).

Although in many large fires the original fuel and the major source of heat and toxic products may be the contents, a significant contribution may be made by construction products. Of great importance in some cases are surface coverings or components with a large surface area such as doors or partitions. Surface coverings may contribute to flashover spread (as in the Dublin Stardust disco fire) and may release a bolus of toxic products very quickly, which may have a serious incapacitating effect on victims. An example would be vinyl wall coverings or the vinyl laminates used in aircraft cabins. Polyvinylchloride releases all its hydrogen chloride at a low-temperature (approximately 250-300 °C), so that as a fire develops and the hot layer reaches this temperature, hydrogen chloride (HCl) may be suddenly released. In another aircraft fire test conducted by the Federal Aviation Administration, high concentrations of HCl and hydrogen fluoride (HF) occurred in the cabin atmosphere before other gases reached toxic levels (see Purser, 1989).

In general, although in some cases fire and heat may eventually kill victims, this is usually preceded by dense, highly toxic smoke that can spread rapidly throughout a space or a building, and it is this that is usually responsible for the initial incapacitation of occupants, as well as being the cause of many deaths.

TABLE 6 Average Concentrations of Toxic and Physical Hazards over 30-Second Periods During Aircraft and Fractional Incapacitating Doses External Fuel/Cabin Fire - Mid Cabin, 1.7 Meters

	0.5 min	1.0 min	1.5 min	2.0 min	2.5 min	3.0 min	3.5 min
	Gas Concentration						
CO (ppm)	8	34	282	1,157	3,326	8,410	19,490
HCN (ppm)	0	10	38	143	340	740	1,380
CO_2 (%)	0.0	0.0	0.4	1.2	2.8	4.1	6.0
O_2 (%)	21	21	21	20	18	16	13
	Fractional Incapacitating Doses						
FED_{co}	0.00	0.00	0.00	0.02	0.06	0.16	0.38
FED_{HCN}	0.00	0.00	0.01	0.06	5.65	> 10	>10
VCO_2	1.00	1.00	1.12	1.31	1.77	2.27	3.26
FED_o	0.00	0.00	0.00	0.00	0.00	0.00	0.01
FED/30s	0.00	0.00	0.00	0.10	10.10	>10	>10
ΣFED	0.00	0.00	0.00	0.11	11.10	> 10	>10
	Radiant Heat Flux						
W/cm^2	0.10	0.12	0.14	0.18	0.23	0.28	0.57

NOTES:
Time to exceed smoke tenability limit: 1 minute 40 seconds.
Time to incapacitation by narcotic gases: 2 minutes 15 seconds.
Time to incapacitation by convected heat: 2 minutes 45 seconds.
Time to tenability limit for radiant heat: 2 minutes 45 seconds.

Effects of irritants:	average respirable particulates 6.7 mg/1,
Over period between 1 and 4 minutes:	average total particulates 11.6 mg/1,
	average HCl concentration 1,027 ppm,
	average HBr concentration 1,228 ppm.

It is considered that the oily, organic-rich, particulate collected, with its very high acid gas content, would be highly irritant and extremely painful to eyes and breathing, causing incapacitation and impairing escape attempts. It is considered likely that these irritants reached high concentrations (approaching 1,000 ppm total acid gases) early in the fire at approximately 1-1.5 minutes, from which time escape capability would be significantly impaired. It is likely that sufficient irritants would be inhaled up to 4 minutes to cause life-threatening post-exposure lung damage.

Table 7 shows the results of another Boeing 707 fuselage test, which was conducted under the same conditions as those used for the test whose results are shown in Table 6, except that a fine water spray mist was applied to the zone of the cabin interior opposite the fuel fire. In contrast to the previous fire, the water mist prevented significant decomposition of the cabin interior materials, so that the cabin remained tenable for up to approximately 7 minutes.

TABLE 7 Average Concentrations of Toxic and Physical Hazards and Fractional Incapacitating Doses over 30 Second Periods During External Fuel and Aircraft Cabin Fire, - Cabin Fire Zone Sprayed with Water Mist - Mid Cabin, 1.7 Meters

	3.0 min	3.5 min	4.0 min	4.5 min	5.0 min	5.5 min	6.0 min
Gas Concentrations							
CO (ppm)	213	239	248	260	316	383	535
HCN (ppm)	4	6	9	9	8	8	8
CO_2 (%)	0.1	0.2	0.2	0.2	0.3	0.3	0.4
O_2 (%)	20.7	20.7	20.7	20.7	20.6	20.6	20.3
Fractional Incapacitating Doses							
FED_{co}	0.004	0.004	0.004	0.004	0.005	0.007	0.009
FED_{HCN}	0.003	0.003	0.003	0.003	0.003	0.003	0.003
VCO_2	1.02	1.04	1.04	1.04	1.07	1.07	1.1
FED_o	0.000	0.000	0.000	0.000	0.000	0.000	0.000
FED/30s	0.007	0.007	0.007	0.007	0.009	0.011	0.013
Σ FED	0.007	0.014	0.021	0.028	0.037	0.048	0.061
FEDs of Convected Heat							
Temp °C	20	20	20	23	26	31	39
FED/30s	0.000	0.000	0.000	0.005	0.001	0.007	0.008
Σ FED	0.000	0.000	0.000	0.005	0.011	0.018	0.026
Radiant Heat Flux							
W/cm²	0.9	0.9	1.0	1.0	1.0	1.0	1.0

NOTES:

Time to exceed smoke tenability limit: 2 minutes.

Time to incapacitation by narcotic gases: no incapacitation.

Time to incapacitation by convected heat: based upon the algorithm for dry or slightly humid air incapacitation would not occur. Based upon work with saturated air, it is considered that conditions would be tenable for up to 7 minutes (end of test). Since this was a zone-sprayed test, there would be no spray droplets falling on the skin.

Time to tenability limit for radiant heat: limit not exceeded, maximum 1.2 kW/m² (at 7 minutes).

Effects of irritants:	average respirable particulates 0.24 mg/1,
Over period between 1 and 4 minutes:	average total particulates 0.65 mg/1,
	average HCl concentration 23 ppm,
	average HBr concentration 0 ppm.

It is considered that the combined concentration of these and other irritants would have some irritant effect on the eyes and respiratory tract, but probably not sufficient to cause serious incapacitation or seriously impair escape attempts, or cause serious post-exposure lung damage. The total particulate concentration is much lower than observed in the nonsprayed and fully sprayed tests. It is considered likely that these irritants reached high concentrations (approaching 1,000 ppm total acid gases) early in the fire at approximately 1-1.5 minutes, from which time escape capability would be significantly impaired. It is likely that sufficient irritants would be inhaled up to 4 minutes to cause life-threatening post-exposure lung damage.

RECOMMENDATIONS TO ENHANCE SURVIVABILITY IN AIRCRAFT FIRE ACCIDENTS

The development of hazardous situations in a fire involves a wide range of factors. These include fire development, from ignition to the post-flashover spread of fire and smoke; toxicity; the interaction of the fire with the structure and with passive and active fire protection; and escape-related factors including detection, warnings, the provision of escape routes, way-finding, physiological and behavioral impairment, and escape movements or rescue. In designing a system to be safe in fire, all these factors should be considered, and the ultimate evaluation of safety depends upon whether it is possible to ensure, by performing a life-threat hazard and risk assessment, that the occupants can reasonably be expected to have escaped before they are exposed to levels of heat and smoke that may endanger health and threaten life.

In the context of aircraft fires, there are a number of strategies that could be adopted to enhance survivability in aircraft fire accidents. The considerations differ somewhat between in-flight fires and post-crash fires.

In-Flight Fires

The foremost considerations with regard to in-flight fires must be prevention, limitation, detection, suppression, and compartmentation. Aircraft materials, design, and construction are all planned with fire prevention in mind. Materials, particularly cabin lining and seating materials, are currently selected with a high fire performance specification in terms of ignitability. Ignitability, flame spread, and heat release characteristics are all very important in terms of fire-initiation and growth. Toxic potency criteria may also be a consideration in terms of materials selection. For fires in concealed spaces, early detection and the provision of suppression systems are very important. Containment and fire stopping is doubly important. First, if the fire occurs in a sealed space it will self-extinguish, and second, penetration of toxic smoke generated in the early stages of the fire into occupied areas is less likely to occur.

Fires involving wire and cable can present a problem in smoldering or small flaming fires due to the organic irritants and acid gases that evolve. Materials with an improved flame propagation and higher decomposition temperature performance may be advantageous, provided that they do not evolve high toxicity products when they are overheated (Purser et al., 1994).

In situations where the cabin or cockpit atmosphere becomes contaminated with smoke from small in-flight fires, it may be important to minimize the inhalation of irritant smoke. This might be done by increasing the rate of cabin air change to reduce smoke concentration, or in extreme cases by using oxygen masks (provided that the fire is not in the cabin).

Consideration should also be given to the psychological effects of being trapped for some hours in an irritant-smoke atmosphere.

Fires on the Ground

If the aircraft is on the ground the main hazard is from rapidly growing fires, of which a post-crash fire involving fuel is the most serious. As shown in Table 6, such fires can render the cabin untenable within a few minutes. The main methods for improving survivability must therefore be to delay the spread of fire into the cabin, and then the fire involvement of the cabin interior, while achieving rapid evacuation. Improved ignitability and fire-growth performance of materials have gone some way towards improving the fire performance of seats and other cabin materials, but large external fuel fires are still capable of igniting cabin materials in a short time. Low-volume water mist systems have been shown to provide a significant benefit in some situations by delaying cabin interior involvement in the fire.

Other problems in this scenario impeding evacuation may be the presence of dense, irritant smoke and high concentrations of hydrogen cyanide and carbon monoxide. The evolution of irritants may be reduced by choosing cabin lining materials that do not evolve high HCl and smoke yields at relatively low- temperatures. It might also be an advantage to avoid or protect materials likely to evolve high yields of HCN, such as polyurethanes.

Other aspects to consider are ways of improving passenger egress. Better protection to avoid physical injury in crashes, less cabin baggage in upper stowage bins, wider aisles and more exits, good low-level lighting and signage, and similar methods might improve movement ability. Improved warnings in case of emergency, such as encouraging passengers to make an escape game plan in advance, could also be beneficial.

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In-Service Performance Criteria for Aircraft Interiors

Hanns-Jöerg Betz[*]

INTRODUCTION

Besides flammability, toxicity, smoke emission, wear-resistance, and other technical requirements that are defined in detailed specifications by the aircraft manufacturers, special requirements out of the service experience had to be incorporated in the design of aircraft interiors. Often the specification requirements do not meet the "in-service requirements criteria." In order to create a comfortable feeling for the passenger the aircraft interior must provide durable performance while showing a clean, pleasing, and comfortable cabin without any visible damage.

INFLUENCE FACTORS TO THE CABIN PERFORMANCE

An ideal airplane interior would have outstanding performance, would not need any maintenance, and would allow a system of servicing that would not damage the furnishings. Unfortunately, up to now and in the near future this is not feasible. Airlines recognize that they are dealing with people and are generally content with the low incidence of vandalism.

There are several factors that influence cabin performance. These include:

- design and manufacturing,
- material performance,
- passengers,
- service personnel, and

EXAMPLES OF PERFORMANCE PROBLEMS

Material Performance

The first thing that passengers notice when they board an airplane is the floor covering. Directly, they can see dirt and wear caused by trolley wheels, shuffling shoes, and uneven floor panels. Panel gaps, moving panels, and washers not properly attached allow bolts to show clear marks on both nontextile and textile floor coverings —especially on nontextile floor coverings that

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are installed in areas prone to corrosion or heavy loads. Slip resistance must be maintained throughout the year, especially in the winter, to provide safety for the passengers and crew. During the winter, floors can be made slippery by residues from anti-icing fluids, increasing the potential for mishaps.

The next items that passengers see and feel are the seats. The performance metric for seat cushion behavior is the indentation hardness. Not apparent to the passengers are the safety-enhancing characteristics of the fire-blocking layers. Aged fire-blocking layers may no longer meet fire-blocking standards as currently specified. Regular tests of used cushions are carried out to maintain confidence in the material performance.

Generally, passengers do not notice inactive bulbs in the lighting system until a specific situation occurs where the lights are needed (e.g., when there is a need for a reading light, passenger signals, or floor path markings). Since it is too late to solve the problem during the flight, the airlines do frequent inspections and repairs of these systems, which create unnecessary costs.

Passengers and Crews

During boarding, passengers may have problems in stowing their hand luggage. The allowable number and size of carry-on bags are defined by the airlines and the International Air Transport Association. Nevertheless, passengers often bring more luggage onboard than allowed. Hand luggage is sometimes too large to fit into the stowage bin opening which results in the use of force to stow the luggage. The consequence is damaged hinges, doors, and structures.

Hard hand luggage or bags with special latches can damage walls and decorative laminates, as they are squeezed through the narrow aisles. Thin laminates and lightweight panels are damaged easily and then have to be repaired.

Toilets are used to dispose of waste paper towels, diapers, beer bottles, plastic glasses, and sometimes passports, which clogs toilets and disturbs the next passenger, who will have an unusable toilet.

REASON FOR PERFORMANCE PROBLEMS

Other reasons for performance problems are caused by servicing and maintenance personnel.

Servicing Personnel

Catering, cargo loading, cleaning, toilet-servicing, and water-servicing personnel are generally low-paid, low-skilled people. After a short training course, they are required to learn "on the job." They are always under time pressure, as they do not want to be responsible for departure delays. When problems occur, they try to solve the problems by themselves without detailed knowledge of the situation (e.g., resetting systems, trying to switch systems, or trying to override a system).

Transporting heavy trolleys with additional parts on top will damage floor panels and floor covering. In cargo compartments, decompression panels are damaged and require repairs.

Maintenance Personnel

Maintenance mechanics are responsible for keeping the cabin in good condition in terms of performance and appearance. Problems are identified using the cabin log book, the technical log book, quick examinations by mechanics during transits, and specified maintenance checks. In the beginning of the service of a new aircraft, the documentation is incomplete and background information on potential problem areas is not available. During this time, the mechanics are learning from experience and on-the-job training, necessitating additional inspections and functional checks to verify that performance has not been compromised.

Design deficiencies cost a significant amount of additional work for the mechanics. The first modifications of the parts improve the situation. If sufficient spare parts are available, the mechanic may exchange the parts without registering a complaint, which allows maintenance trends or poor performance to remain unsubstantiated.

PERFORMANCE CRITERIA The appearance and function of the cabin needs to be maintained to a high standard. The aircraft cabin is regularly checked according to maintenance checks, intervals, and tasks. The maintenance checks take the following items into consideration:

- continuous safety,
- quality for passengers,
- materials, and
- costs per part.

Continuous Safety

Safety in an aircraft cabin is mandatory. Therefore, regular checks are required by the crews and by the mechanics. At the beginning of the flight, all passengers are asked to become familiar with in-flight safety requirements and evacuation requirements.

Flammability Requirements

In the case of component flammability, it is difficult to ensure the quality and compliance with the applicable rules. Therefore, it is necessary to only allow the use of materials that meet regulatory requirements for flammability.

One means to ensure continued compliance with flammability requirements is to have spares in storage of all parts that may be damaged. Since this is obviously not feasible, the mechanic must have the materials and methods available to repair parts that allow continued compliance with performance requirements. Repair materials and spare parts must meet the latest standard of flammability requirements. There should also be assurance that the component design is tolerant of an acceptable level of damage without influence on the flammability requirements.

Prevention of Cabin Malfunction

Damage may occur due to improperly latched bins, stowed and latched trolleys, and ovens. Therefore, proper checks of all latches before and during flight need to be performed by the cabin crew. Bins not properly locked may cause damage and could represent a danger to passengers.

Quality for Passengers

To achieve the maximum comfort for the passengers and reduce maintenance, improvements in aircraft interior seats, seat cushions, galleys, lavatory systems, entertainment, cabin lighting systems, and air-conditioning systems are needed.

Ideally, seats should not have to be inspected at all and should always function properly and provide complete comfort. Colors, fabrics, and surfaces are chosen that hide dirt and are easily cleaned. Ashtrays are designed to be cleaned without any damage. Seat cushions are designed to fit in the seat structure without internal tearing.

The appearance of a new replacement part should not be significantly different from the original installation. Repairs of minor damage need to be easily hidden.

A significant amount of maintenance and a number of modifications are required to keep cabin systems, such as lavatories, water systems, and entertainment systems, functioning. In case of system problems during flights, notification of the crew and remediation should occur without disruption of passengers.

Airlines need to continue to improve the comfort and convenience of travel for passengers. Therefore, Lufthansa and other airlines are searching for new developments or features for in-flight entertainment and other items to better please our passengers. It is also important to heed trends in passengers' demands or complaints.

Materials

The technical performance requirements for the cabin materials are defined in detailed specifications. Some of the characteristics controlled in materials specifications include:

- flammability,
- low-cost producibility,
- resistance to aging,
- color stability and reproducibility,
- mechanical properties,
- ease of repair, and
- optimized weight.

The weight has an important influence on the fuel costs, payload range, and performance.

Costs per Part

Many Lufthansa customers complain about high fares for flights. We are often shocked as well with the cost of an interior part. But there are significant nonrecurring and certification costs associated with the development of a part to be installed in an aircraft. Also, the manufacturer has to guarantee excellent product quality and quality control that meet the requirements of the specification. In addition to these costs, the airline has to account for the maintenance, overhaul costs, part service life, and product improvements. These additional costs may reduce the performance tremendously. Having parts in the shop for repair too often results in modification or exchange of the part. Service and maintenance experience for cabin components are reported to the supplier and aircraft manufacturer. These experiences may lead to modifications to improve the performance. Product support is very important to enable keeping parts in good condition.

Maintenance and In-Service Costs

Maintenance actions are always seen in connection with high operating costs. These activities range from daily monitoring to an overhaul or D-Check, which has to be performed, in most cases, every 5 to 6 years. At this time, a 747 will have carried about 200,000 to 300,000 passengers per year. Therefore, the frequency of the maintenance inspections is important to achieve a positive result. For economic reasons, it is necessary to reduce the duration and downtime of the airplane. To reduce the downtime, it is necessary to either increase the manpower or to make maintenance activities easy. Accessibility of parts for maintenance actions is very important. Otherwise, delays will result, and passengers will become disappointed or angry. Further delays could lead to other problems such as rotation problems, disruption of inspection intervals of other airplanes, and cancellation of flights (with airline responsibility for hotel accommodations).

Airlines are looking to reduce the manpower needed to perform maintenance and to perform the work with lower-qualified personnel. These trends reinforce the need to improve cabin design and materials performance to a point where, instead of performing maintenance, ground personnel need only check the function and appearance of the cabin.

CONCLUSION

Aircraft cabin performance criteria are influenced by

- frequency of required actions,
- material,
- people, and
- design.

Cost and quality need to be optimized for

- weight, part costs, and in-service costs;
- safety and quality for passengers; and
- lifetime costs.

Airlines need a passenger-pleasing and safe airplane at all times with reductions in required maintenance.

Design of Aircraft Interior

*Swen J. Schaich**

Means of transport serve not only to convey passengers from a place of departure over a certain distance to a place of destination. During the time of travel, further functions and performances must be performed:

- accommodation in passenger cabin;
- protection of passengers from harmful impact;
- serving of food;
- removal of waste, etc.; and
- entertainment.

With respect to these further functions, special demands are made on commercial aircraft. Because of the high cost of investment, the operators aim to put the aircraft to maximum use. This is achieved by the adaptability of the means of transport and a wide range of services offered. However, the scope of variation is considerably restricted by specifications meeting physical, economic-technical, and safety requirements. In a way that does not apply to any other means of transport, the weight of the aircraft is of paramount importance in economic considerations. Where air traffic is concerned, a particularly careful comparison of the required expenditure with the expected benefit is therefore called for.

The interior furnishing of Airbus cabins includes all components that are installed between the dividing wall to the cockpit and the pressure bulkhead in the rear fuselage. This applies to the upper deck, where the passengers are accommodated, as well as to the cargo compartments below. The equipment and furnishings include floor panels and carpeting, lower sidewall panels, upper sidewall panels, overhead stowage compartments, service channel, ceiling panels, dividers, lighting, air-conditioning outlets (blowers, ventilation grids, etc.), passenger seats, flight attendant seats, flight attendant work stations, galleys, lavatories, stowages, passenger information signs, and emergency equipment.

These standard furnishings are supplemented by optional items that are installed at the request of a particular airline, such as entertainment systems (audio, video), special provisions for the disabled, sleeping compartments, additional galleys and lavatories, more comprehensive emergency kits, and stairways.

Due to different arrangements and variations in the number of items, an almost unlimited variety of interior design configurations is conceivable. This conceivable variety, however, is in actuality restricted by the installation conditions, mutual overlappings, feasibility, installability, and, not least, safety considerations.

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FUNCTIONS AND PERFORMANCES OF AIRCRAFT INTERIOR

INTERIOR FURNISHING REQUIREMENTS

The aim of aircraft interior design is to create such conditions on board commercial aircraft as are expected by the passengers. To achieve this objective, many requirements must be met. These can be subdivided into two categories:

- absolutely necessary measures, of vital importance for the passengers; and
- options that go beyond mere transportation and serve to create pleasant and comfortable traveling conditions.

Looked at another way these requirements can be viewed as including those that provide for (a) the accommodation of passengers, (b) the protection of passengers, (c) passenger services, and (d) passenger entertainment.

Accommodation of Passengers In the past, it was common procedure for aerodynamicists, structure specialists, system engineers, etc., to build an aircraft to meet the needs primarily of their respective disciplines. The space available after all systems had been installed was then dedicated to passengers and furnishings in the most advantageous manner.

After years of this approach, the mind-set of the development engineers has finally changed, so that accommodating the passengers now means to design the cabin layout according to the passengers' needs. The cabin layout must allow the demands for maximum transport capacity (high passenger density) or maximum comfort (low passenger density) to be realized. Or, to put it more simply, the means of transport-the aircraft-and basis for a slightly graded passenger comfort, is built around the cabin, with due consideration, of course, to the physical and technical general conditions applying to an aircraft. In addition to the arrangement of seats, aisles, and escape routes, passenger accommodation also includes stowage space for hand luggage and a coat room. The requirements increase with the flight time; if several different climatic zones are traversed, the corresponding clothing is needed, as are reading matter, work documents, and games to help pass the time and toiletry articles for refreshment.

On long-distance flights, passengers will ask for facilities for resting. The demand is due to business executives' needing rest, the transport of disabled, sick, or injured persons, and the need to accommodate replacement crews. The sleeper seats in common use today fulfill these expectations only in part. It is for this reason that regular rest compartments are now offered for crews, for instance.

Protection of Passengers

The aircraft interior in its entirety is laid out to protect passengers during their stay on board from all impact hazards likely to affect their well-being. The interior furnishing components and the service systems are therefore laid out not only to make the stay on board the aircraft pleasant and comfortable but to provide maximum safety from all kinds of risks both during normal operation and in emergency situations.

The function of the passenger seat is to accommodate the passenger and to afford a comfortable position for the duration of the flight. A belt serves to retain and keep the passenger from slipping out of the seat, for instance, during sleep, or in the event of gusts, turbulences, or rough landings.

Reasonably dimensioned longitudinal and transverse aisles provide for interference-free traffic during boarding and leaving as well as during flight. These areas also serve as escape routes.

Stowage compartments above the passenger seats receive the hand luggage. They can be locked and thus prevent pieces of luggage from dropping onto the passengers in all flight conditions. Dropping luggage presents a double hazard: injury to the passengers by immediate impact, or obstruction or blocking of escape routes.

The cabin lighting system can, in connection with an emergency lighting system, help to avoid all sorts of mishaps.

Since the equipment installed in the galleys and the provisions kept there can have a considerable weight, dual safety features are installed to prevent their uncontrolled movement. Throughout the cabin, passenger information signs and lighted signs are fitted that either provide information regarding the use of facilities (e.g., pictograms) or request a certain passenger behavior with the aim of minimizing safety hazards (e.g., "FASTEN SEAT BELT").

The air-conditioning and cabin pressure control system protects the passengers from the effects of temperature, humidity, and flight altitude and supplies them with breathing air under conditions that resemble as closely as possible those on the ground.

The entrance areas and the individual classes are separated by dividers that protect the passengers seated next to the doors from draft and heavy rain entering the cabin while passengers board and leave the aircraft. By suitable arrangement and design, dividers also break the long tube of the cabin down into sections that are furnished in accordance with the respective class standard. Naturally, the dividers are also used for other purposes, such as promoting the corporate image of the airline, advertising, providing literature pockets, or the reception of folding baby bassinets.

All components inside the cabin must be made from approved materials that in case of fire emit only small amounts of smoke and toxic gases and release only a limited amount of thermal energy (ATS 1000, Heat Release 65/65). Only such types of construction are used that, if mechanical failure occurs, do not present an additional risk of injury on account of the structure of the fracture.

All these functions are dependent on an aircraft structure that allows installation of all interior furnishing components, as well as the service systems, and that is capable of supporting all occurring loads.

Naturally, the cabin interior must offer optimal protection for the passengers, especially under crash conditions and provide means that are absolutely necessary to survival, such as oxygen systems, emergency exits and emergency escape slides, and fire-fighting equipment.

In summary, it can be said that both active and passive safety measures are taken to protect the passengers:

- Passive features are those that exclude safety hazards (e.g., nonflammable materials).
- Active features are those that reduce or eliminate existing dangers (e.g., fire extinguishers).

The interior furnishing components are therefore developed on the basis of the following criteria:

- minimization of risk potential during use, and
- provisions to reduce or eliminate the risk of accidents in dangerous situations.

As with all other features, the protection of passengers, in particular from accidents, can also be extended and improved. However, such schemes make great demands on engineers from various different technical areas and involve considerable costs for development, manufacture, and sometimes even use.

Passenger Services

Depending on the specific flight, the passengers will be on board the aircraft for a longer or shorter period. During this time, at least the minimum needs of the passengers must be satisfied. But a further spectrum of services that goes beyond the very basic needs can be offered by the airlines to make traveling an attractive and pleasant experience.

This means not only the serving of food and drinks in varying quality and selection by attentive flight attendants but also special offers that accommodate individuals' wishes and needs. Here, emerging trends must be carefully observed and analyzed.

The trends do not develop uniformly. On the one hand, increasingly exclusive service facilities are demanded and supplied, and on the other hand, inexpensive flights where service is reduced to the absolute minimum are on the increase.

Because the passengers pay special attention to the services offered, the airlines formulate particularly varied requirements in order to present their company-specific image.

Passenger Entertainment

Contrary to travel in ground-supported means of transport, flying usually offers, with the exception of take-off and landing, hardly any welcome diversion. Because the cruise flight takes place at high altitude, it is difficult to make out any details on the ground, and vision is often impeded by clouds and mist. In addition, the number of window seats is relatively small compared to the number of seats per seat row.

Although entertainment is not counted among the basic human needs, because of worldwide competition, no airline can afford nowadays not to offer these services.

The range of activities offered must be adapted to the operational concept of the aircraft, the flight time, the image of the airline, and in particular the expectations of the passengers. It begins with the distribution of magazines and includes audio and video programs, computer games or complex information systems. These information systems allow the passengers to use information, work, or entertainment programs according to their personal preference. As in the serving of food, the trend here is also for "à la carte."

Finally, business executives require communication services. The first and business classes need to be equipped, besides with telephones, with telefax and data services, to be supplemented by a secretariat if necessary.

DETERMINING FACTORS

Customer Requests and Feasibility

Every airline faces the problem of maintaining a company-specific image that uniquely distinguishes it from its competitors. The exterior appearance of the aircraft provides a first impression of the airlines' corporate image, although in most airports passengers are checked in via closed passenger bridges.

The interior design of the passenger cabin is also of the utmost importance. It is not merely a question of realizing the services described above; the airlines are also demanding ways and means to present their own specific concept of passenger service, which again means that every airline demands its specifically conceived interior design configuration. For the aircraft manufacturer, this means that standard solutions are not sufficient to meet the actual requirements. In other words, the sales prospects are largely dependent on the degree to which the interior design of the passenger cabin can be adapted to comply with the ideas and wishes of the customer. The aircraft manufacturer's response is therefore to develop types of aircraft that permit a high degree of flexibility where configuration and design of the interior components are concerned. At the same time, the costs for design, manufacture, and installation are kept within certain reasonable limits in order to achieve relatively short and scheduled planning and installation periods, and prices that the market will be prepared to pay.

Types of Construction and Materials

All aircraft components are designed according to lightweight construction principles because of the direct impact this has on the payload that can be transported. In the area of interior design, the requirements are very complex since several functions must be fulfilled all at once:

- stiffness—lightweight construction and high-stiffness materials to achieve a maximum payload;
- safety—protection of passengers during flight and in emergency situations, and moderation of the results of accidents;
- design and color—design that follows function and is esthetically satisfying, as well as suitable surface structure and color scheme;
- durability—resistance to wear in the daily contact with passengers, and resistance to environmental conditions such as ozone, ultraviolet radiation, cigarette smoke, and caustic cleaning agents;
- hygiene—dirt-resistant and easy-care surfaces, resistance to food and kindred goods (tobacco, alcohol) and compatibility with cleaning agents and disinfectants; and
- handling—design and instructions suitable in form, fit, and function for the "standard passenger" as well as passengers with special needs, such as disabled people and children.

In view of the multiple requirements, composite and hybrid structures are of particular importance. Sandwich structures are of high strength and retain their shape. Metallic materials are practically no longer used, except for mechanically and thermally highly stressed components. The primary structures are covered with preformed parts and then individually finished by means of decor foils, varnishes, or textiles.

Large components are treated in a similar way. Temperature-resistant layers for flammable materials improve the resistance to fire (fire-blocking foam layer for seat cushions).

By embedding materials capable of dangerous fracturing behavior in flexible material, the risk of injury in the case of accidents is reduced.

Since the passengers have direct access to most of the interior furnishing components, the wear to which these components are subject (through faulty operation, lack of understanding, malice, etc.) and the resulting failures and necessary replacement have to be taken into account. Assembly techniques that allow quick installation with the aid of only a few tools are therefore very important in order to avoid costly turn-around times. The elements used in this connection are mainly of the plug-in, snap, locking, or clamping type, which calls for a high degree of accuracy to size and inherent stability of the component parts.

Special measures are taken where resistance to fire is concerned, since a fire puts the passengers in extreme danger. There are two basic scenarios:

In-flight fire. A fire breaks out during the flight. The fire-fighting provisions must allow extinguishing the fire or slowing down the rate of propagation so that the nearest airport can be reached. The main objective must be to maintain the capability to fly. Because of the passengers, the smoke densities and the toxic constituents of the combustion gases must not exceed certain values.

Post-crash fire. Emergency landings may be accompanied by fires that are the result of fuel leaked from the wings or fuselage in the wake of the crash. In this case, too, the fire propagation must be slowed down to give all passengers maximum opportunity to leave the aircraft. However, this is only possible if the passengers are not impeded in their movements by smoke, toxic combustion products, or heat.

The technical instructions refer to the release of thermal energy, smoke emission, and toxic gas components. For this reason, many interior furnishing components have had to be replaced at great cost with new materials. Materials such as polyvinylchloride (PVC), acrylonitrile-butadiene-styrene (ABS), or epoxy resins must no longer be used in the cabin; they have been replaced mainly with polyetherimide (PEI), phenolic resins, and others.

By joint efforts on the part of aircraft manufacturers' interior design departments and material development departments, new materials that comply with the tightened limit values have been introduced.

COMMERCIAL ASPECTS

The discussion above may give rise to the impression that everything connected with the aircraft interior only causes considerable problems or rising costs for manufacturer and operator alike. It is true that the costs are high. But this impression is put into perspective if one keeps in mind that the interior design, apart from the service, is the most effective means an airline has for self-representation; in other words, the interior design is a marketing instrument of the highest order and must therefore express the airline's excellence.

The manufacturer of interior furnishing components has a sales market that lasts for the whole utilization phase, a period of 20 to 30 years. Many components need to be replaced during this time for reasons of wear, modification, modernization, or conversion.

Proportion of Interior Design Costs Compared to Overall Costs

The following data give an idea of the financial dimensions behind an aircraft interior: quoted on the basis of the overall manufacturing costs for the Airbus A340 long-range aircraft;

- Interior furnishing of the cabin represents approximately 8.5 percent of the overall manufacturing costs of the aircraft.
- Interior furnishing of cargo compartments represents approximately 1.5 percent of the overall manufacturing costs of the aircraft.

In referring to interior furnishing of the cabin and cargo compartments, there are about 8,000 different assemblies, about half of which must be modified to comply with the respective wishes of customers.

Effect of Interior Furnishing on Profitability

Like other companies, the airlines must aim to make a profit. With few exceptions (e.g., cargo airlines), the largest share of their turnover is realized by the transport of passengers. Depending on the routes, however, earnings can also be improved by transporting cargo in addition to the passengers' luggage. Principally, there are two ways to boost turnover:

1. Increasing the transport capacity. The cabin is laid out to accommodate the maximum number of passengers. Comfort and service are minor considerations. In order to achieve as nearly as possible full-capacity utilization, low-price tickets are offered (as, e.g., by charter airlines).
2. Increasing the transport quality. The passengers are offered services and conveniences that exceed the usual standard. Here, a group of travelers is addressed who enjoy special services and are prepared to pay for it.

In all instances, the strategy of the airline must be reflected in the cabin layout. The custom-designed interior components must be evaluated with a view to profitability, that is, in terms of additional income to be realized versus the amount of capital investment necessary to achieve it.

An example of the above may be the transfer of service facilities to the underfloor area. For example, moving the lavatories to the aft cargo compartment may free additional space on the main deck for other purposes.

This example shows very clearly that the cabin layout can significantly influence the profitability of an aircraft.

Conversions or Second Interior Furnishing Sets

Commercial aircraft are high-technology industrial assets that will be in service for long periods (20 to 30 years). During such a long time, the requirements regarding the interior furnishing of the cabin are subject to many changes due to such factors as

- change of ownership,
- modified service concept on account of different flight routes,
- altered sociological structure of passengers,
- technological progress, and
- modernization.

The basic cabin layout must therefore incorporate a high degree of flexibility in order to provide the preconditions required for adaptation to changed circumstances.

The interior furnishing components of an aircraft have a shorter life cycle compared to the airframe. This results from wear (the constant use by passengers) and also from changes in fashion that make the design of a cabin layout appear outmoded. For these reasons several interior furnishing "sets" for the same aircraft may be required during the life cycle of an airframe. Such conversions need to be performed without major modifications to the aircraft, that is, without essential alterations to the structure (modular system, families of parts).

Further Development

On long-distance flights, the cargo compartments cannot be used, or can be used only in part, for transporting goods because of the payload limitations effective for certain distances. If an airline wishes then to avoid transporting empty stowage, the utilization spectrum of the cargo compartments can be enlarged by transferring service facilities for the passengers from the cabin to the underfloor area. The following several functions may be realized in the underfloor area:

- storage space for the provisioning of food and beverages (catering),
- galleys,
- lavatories,
- crew restrooms, and
- passenger lounges.

Through separation of the passenger and service areas, the passengers on the main deck will no longer be subject to molestations in connection with galleys and lavatories (traffic, unrest, noises, odors, etc.) and will have greater freedom of movement. This will enhance passenger transport quality. Passenger transport capacity also can be enhanced by installing additional passenger seats in the areas that have become available.

This type of utilization extension is the more effective the more service facilities are moved. The advantages offered by the shifting of cabin functions are not restricted to long-distance flights. They are always useful where, without changing the outer dimensions of the aircraft, more space is to be made available for cabin functions. However, cargo compartments will have to be retained to accommodate the passengers' luggage.

Processing and Manufacturing of Interior Components

*Hans-Dieter Berg**

INTRODUCTION

The heading "Processing and Manufacturing of Interior Components" comprises a broad range of processing of very different materials, the majority of which are nonmetallic. The diversity of these materials and the components in which they are used requires considerable variance in manufacturing techniques.

In addition to technical requirements, a large proportion of interior components must also meet decorative requirements. In most cases, the process of decorating is a separate operation that must be repeatable (for purposes of repair and refurbishment) for the large-area components of the passenger cabin (e.g., sidewalls, walls, and stowage bin doors).

Therefore, interior components generally consist of a combination of different materials and semifinished products. An example of a simple structure is components manufactured by injection moulding (e.g., parts of the passenger service unit) where component function and decorative aspect are combined by direct dyeing.

An example of a complex structure is decorative sandwich panels. Today, the major part of the passenger cabin consists of this type of components. Normally, they are made of a sandwich structure with a rear and front top layer of fiber-reinforced plastics (e.g., phenolic resin) with a Nomex® hexagonal honeycomb core. Very often, the decoration comprises decorative laminates, which again consist of several layers (PVF foils, embossing, paints, adhesives).

If we consider the fire/smoke toxicity (FST) behavior of such a structure, it is first of all important that the specifications require the inspection of the overall structure. The FST behavior of the individual elements, such as that of fiber composites in such a sandwich structure, is only a part of the overall FST result. We know, for example, that an excellent heat release result for a prepreg system is not reflected by the heat release of the overall system. On the other hand, a heat release result measured on an individual laminate can clearly exceed the limit value of 65/65 $(\mathrm{kW \cdot min/m^2})/(\mathrm{kW/m^2})$ without the limit value of the overall structure being exceeded.

It is also known that different manufacturing processes, for example the process for manufacturing a closed sandwich panel, can result in completely different heat release values although identical materials are used. A sandwich panel, such as for a cabin partition, manufactured in a vacuum process, normally shows lower results than an identical panel manufactured in a multistage press. Furthermore, this phenomenon depends on aging.

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These interrelations clearly show that the manufacture of interior components that are subject to the various FST requirements can be successfully performed only in close cooperation between the developers of materials and the suppliers, designers, materials and process engineers, and production departments of the aircraft manufacturers.

There will be other challenges in the future that will make this process of optimizing the material properties, the processing methods, and component performance even more complex. In the first place, this concerns the necessity to reduce manufacturing costs for the interior by 30 percent and more, a requirement that is implied by the passenger aircraft market. Furthermore, a weight reduction of approximately 10 percent is also expected for the interior for reasons of operating costs and environmental protection (fuel consumption). Added to this are increasing technical requirements and, above all, increasing requirements with regard to human safety, which means not only the safety of passengers in the case of a fire but also the health of those people working in the production department. Last but not least, the question of future disposal of interior components and materials remains to be answered.

The above-stated objectives can surely no longer be achieved by marginally improving state-of-the-art materials and processing methods; it is necessary to achieve completely new solutions which, in a way, permit leaps in development.

STATE-OF-THE-ART PROCESSING AND MANUFACTURING

This section is a summary of materials as well as processing and manufacturing techniques used today. It is obvious that materials and processes are closely related in plastics processing, so that one cannot be described without also dealing with the other.

In this case, the term "interior" will be limited to the passenger cabin, the cargo compartment, cockpit, lavatories, and galleys. Equipment parts will only be mentioned in passing.

A look at the interior of today's wide-body aircraft shows that more than 80 percent of the passenger cabin interior consists of sandwich structures mainly comprising fiber-reinforced phenolic resin top layers with Nomex® honeycomb cores and a decoration of decorative laminates, simple PVF foil, textiles, or varnishes. The manufacturing techniques typical for these components are described below.

Flat Sandwich Structures

The following components are typical:

- floor panels,
- partitions,
- walls (galleys, lavatories), and
- cargo liners.

The most common manufacturing process for these parts is "one-shot curing" in a flat press. Often, multistage presses are used. The prepregs are incorporated in the structure in "wet" condition and are cured on the sandwich core. Normally, the matrix resin is simultaneously used as adhesive for honeycomb bonding.

Individual components can be cured in separate fixtures or several components simultaneously in the so-called "multitooling" process; in the latter case, the individual components are subsequently cut out of large panels. It is possible to implement edge sealing by previous incorporation of potting compounds or foam parts. Subsequent milling-out of the honeycomb in the edge area and filling are also common.

Metallic and nonmetallic reinforcements can be installed or subsequently incorporated in the consolidated panel (e.g., inserts for attachment). The curing conditions are as follows: cure temperature—120-180 °C; cure time—30-90 min; cure pressure—$\geq$ 3 bars.

Curved Sandwich Structures

The following components are typical:

- window panels,
- ceiling panels,
- stowage bins (parts),
- stowage bin doors, and
- door fairings.

These parts, too, are mainly manufactured in the one-shot curing process. The most common process for high production rates is the "crushed core" process. The "wet" prepreg of the front and rear top layer as well as the Nomex® honeycomb core, and, if necessary, inserts and reinforcements, are placed in a heated, divided press tool; the press tool is then completely closed. In this case, the honeycomb core is given a thickness oversize of up to 30-40 percent.

When the fixture is closed, the Nomex® honeycomb is inevitably crushed, simultaneously building up an increased pressure acting against the top layers, which results in considerably improved surfaces for polycondensated phenolic systems as compared to, for example, normal pressing processes.

A similar process is the "package" process during which all materials are also placed "wet in wet" in a divisible closed, heated fixture without crushing the honeycomb.

The cure times for the techniques stated are approximately 10-15 minutes, the cure temperatures up to 175 ° *C.* The cure pressures can partially exceed 20 bars.

The conventional autoclave technique or the vacuum-bag-furnace technique, too, can be used for curved components, as described above, which are to be manufactured only in small quantities.

Decoration

Conventional decoration procedures are the application of decorative varnishes, decorative foils, or textiles. In exceptional cases, other materials can also be applied, such as leather and wood imitations. They are limited by the FST requirements. If required, the component surface is filled and ground or activated.

Decorative varnish is normally applied in three steps: First, a filler is sprayed and ground; then a smooth coating varnish is sprayed; finally, a structural top varnish is applied.

The procedure for the application of decorative foils depends on

- whether the foils have already been provided with adhesive or not, and
- whether a heat-activated or a pressure-sensitive adhesive is used.

If a heat-activated adhesive is used-independent of whether it is applied to the component or provided on the decorative foil-it is heated by a radiant heater field and the foil is pressed onto the component by means of a vacuum bag. The application temperatures are approximately 85-105 °C, the holding time approximately 3-7 minutes.

A pressure-sensitive adhesive is often used for flat and very large components or in the case of repairs; it can be applied, for example, by pressing with a rubber roll.

The simplest form of application of a decoration is by single-layer foil, e.g., a PVF foil, which can also be dyed. These foils can be placed directly in the fixtures for curing of sandwich components and are bonded by the matrix resin.

Textiles used for decoration are mostly applied by pressure-sensitive adhesives or by dispersion adhesives curing at room temperature; the procedure corresponds to the one used for the application of decorative foils.

Monolithic fiber composites, with thermosetting or thermoplastic matrix systems, as well as thermoplastic thermoformed parts and also injection moulding parts are used in addition to sandwich structures.

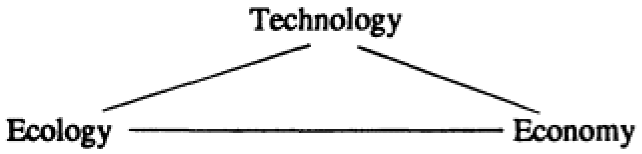
Interior parts of thermosetting composites are manufactured by the conventional press, autoclave or vacuum-bag techniques. Thermoplastic composites processed by thermoforming or folding technique with local heating are also used to a limited degree. The decoration of these parts is performed analogously to the processes described for sandwich parts.

Thermoplastic thermoformed parts (e.g., door fairings) or injection moulding parts (e.g., passenger service units) are normally directly dyed and provided with the desired surface structures. But for decoration purposes, it may be necessary also to varnish these thermoplastic parts.

The processing techniques correspond to the standard processes for these materials. Last but not least, metallic parts should also be mentioned; however, their use is limited. Depending on their application, these parts are decorated with decorative foils, varnishes, or textiles according to the processes described.

FUTURE DEVELOPMENTS IN PROCESSING AND MANUFACTURING

When thinking about future developments with regard to processing and manufacturing, the tensions inherent in the following triangular relation must be accepted:



None of these three fields can any longer be considered separately. It will only be possible to implement well-balanced overall solutions. Specifically, improving the economy of the production of interior components by new manufacturing technologies will no longer be possible without considering effects on the environment in its broadest sense (e.g., the implications for waste disposal and for industrial and health protection). On the other hand, investments in the processing of environmentally acceptable products may well be a sales argument additional to those of the relevant competitive advantages and economic effects.

The above-stated three cornerstones that will frame future developments are already perceptible today in the field of processes and manufacturing procedures for interior components.

Economic and Technological Developments

The market situation requires a drastic reduction of the manufacturing costs for aircraft and thus of the costs for their interior in the future. Developments on the interior sector considered here will focus on the large-area sandwich structure of sidewall panels, ceiling panels, stowage bins, partitions, and walls for galleys and lavatories due to their high share of the interior.

The reduction of the flow times for manufacture and the significant simplification and mechanization of assembly sequences offer an important potential for the reduction of manufacturing costs. However, as far as correlations to passenger safety in the case of fire are of interest in this connection, developments with an effect on the materials and the component configuration are more important.

From today's point of view, there will be no alternative to the basic sandwich design, even in the future. For weight reasons, the sandwich design will remain necessary, in particular for the even larger passenger aircraft being discussed today (600 and more passengers). This type of structure simply offers weight optimization at a high stiffness level for the large-area interior parts that are subjected to comparatively small loading. It is evident that future manufacturing technologies must be based on such a construction. The potential cost reduction can be found in the application of new matrix systems, new core materials, procedures for integration of the decoration into component manufacture, simplified designs, and integral manufacturing techniques for the reduction of assembly work. In particular,

- The new matrix systems should require lower cure temperatures, shorter cure times, and lower cure pressures, and they should be storable at room temperature.
- The potential for using catalytically curing resins must be applied to interior components.
- Lower cure pressures can be used for significant cost reductions in the preparation of tools.
- The application of foams as an alternative to Nomex® honeycomb cores in structural areas that are less critical with regard to structure mechanics offers cost reduction potentials.
- The expenditure for decorations can be reduced by using dyed thermoplastic top-layer materials for sandwich components provided with surface structures.
- Simplified designs and integral manufacturing techniques permit, for example, the manufacture of the essential body of a stowage bin from a flat semifinished sandwich product by special folding technique.

In the area of monolithic components, alternative technologies such as the resin transfer moulding or the resin film infusion process can also be reviewed for their cost reduction potential.

It is evident that thermoplastic thermoforming materials and injection moulding materials are increasingly being used for these components in the established processes.

Ecological Aspects

As pointed out above, development will no longer be exclusively oriented towards economical and technological aspects. The use of working substances considered too dangerous will be more and more restrained. Carcinogenic, mutagenic, and teratogenic products, as well as products harmful to the environment, will be removed step by step from production. In the future, there will no longer be any CFCs, halogenated hydrocarbons, or solvents. Fire retardants such as antimony trioxide or toxic bromine compounds will be replaced by products that are less dangerous to health. On a longer-term basis, the replacement of phenolformaldehyde resins will also be necessary.

Today, the disposal of waste from plastics manufacture has already become a considerable cost factor. Major efforts are presently being made in this area to find cost-reducing solutions. One possibility is to recycle these products. On a long-term basis, however, materials and processes that offer unproblematic parallel disposal will have to be put into place.

CONCLUSION

Identifying trends and directions in aircraft fire safety and suggesting promising research directions requires that those engaged in processing and manufacturing recognize and accept the inherent mutual tensions between technological, ecological, and economic demands. None of these three fields can any longer be considered separately; it will only be possible to implement well-balanced overall solutions. The task of balancing boundary conditions and effects that are partly contradictory, however, is becoming more complex instead of simpler. All participants must therefore cooperate closely to meet this challenge.

PART II

WORKSHOP SUMMARY

The overall objectives of the workshop of the International Conference on Fire and Smoke Resistant Materials were to:

- identify promising technologies most likely to lead to improvements in fire resistance of future aircraft interiors; characterize the state of development of these promising technologies;
- describe the drivers for, or barriers against, the development of improved materials for interiors; and
- suggest objectives for the Federal Aviation Administration long-term research program to facilitate the development of new materials for future aircraft interiors.

The workshop participants were divided into four break-out sessions: Toxicity, Fire Performance Parameters, Drivers for Materials Development, and New Materials Technology. Summaries of issues identified in these sessions follow. The workshop summaries reflect the views and opinions of the individuals who participated in the sessions. These views have not been subjected to review and do not represent the position of the committee of the National Research Council that organized the workshop.

Session I:

Toxicity

SESSION OBJECTIVES

Characterize current fire-toxicity considerations and suggest how these considerations should change in the future.

PARTICIPANTS

Chair:	Stephanie Skaggs, *New Mexico Engineering Research Institute*
Committee:	Barbara Levin, *National Institute of Standards and Technology*
Participants:	Gary Burns, *Dow Corning*
	Daniel Caldwell, *U.S. Army*
	Marcelo Hirschler, *Safety Engineering Labs*
	Thomas Murray, *Boeing Commercial Airplane Group*
	David Purser, *Fire Research Station*
	Henry Roux, *Roux International*
	Chuck Williamson, *General Plastics Manufacturing Co.*

SESSION REPORT

The following views and suggestions were presented by one or more participants in this session. Although the workshop session focused on toxicity, several participants stressed that toxicity is only one aspect of the total fire hazard. Issues surrounding fire toxicity considerations should be product-driven (as opposed to materials-driven) and scenario-specific. New materials should be designed such that toxicity of the product is never the limiting factor influencing survival in a fire scenario.

The two key scenarios to consider include:

- post-crash or external pool fires, and
- concealed in-flight fires.

Excluded as major hazards were fires on unoccupied aircraft (not in revenue service) or visible in-flight cabin fires.

There is a great deal of knowledge that currently exists as a result of previous toxicological research. This information can be used to validate toxicity models.

Current Toxicity Criteria and Characterization Methods

There are currently no regulations establishing general toxicity criteria for individual products for aircraft. No general toxicity criteria are needed, rather a holistic "life-threat criterion" that includes the entire fire environment should be considered.

While many toxicity characterization methods exist, there is currently no one test that adequately meets all needs.

Toxicity Goals for Long-Term Research

The primary criterion for long-term research in toxicology is that toxic hazards in end use should not be the limiting factor of any product. For aircraft interior applications, the criteria require that toxicity not control escape time (i.e., the time available for escape is greater than the time required for escape).

In order to facilitate evaluation of new materials, it is important to develop small-scale tests that have large-scale relevance.

Needed Development in Materials Evaluation and Characterization

Participants in this session suggested the following would be useful in evaluating and characterizing new materials.

- Design characterization methods that relate to real scenarios (post-crash or concealed in-flight).
- Consider lethality as the primary criterion. Also consider the possible effects of incapacitation and long-term effects of acute one-time exposures, such as immunological dysfunction, allergic reactions, teratogenicity, mutagenicity, and carcinogenicity.
- Validate small-scale tests against large-scale scenarios.
- Consider relevant toxic decomposition gases (narcotics, asphyxiants, irritants), as well as smoke obscuration and heat.
- Include analytical characterization and model prediction, followed by a limited bioassay proof test using animals that best represent human responses.
- Incorporate heat, hot-water vapor, and particulates into predictive toxicity potency models (e.g., N-gas and FED [fractional effective dose]).
- Develop a toxicity profile for decomposition products that includes concentration, effects, and interactions.

Long-Term Research

The participants in the Toxicity session had the following suggestions for long-term research.

- Identify scenario-specific, product-driven characterization methods that are based on performance requirements relevant to human survivability.
- Validate that bench-scale characterization methods adequately represent larger-scale tests of components or representative cabin areas (e.g., seats, row of seats, full cabin).
- Enhance current models (N-gas and FED) to consider the toxicological effects of heat, hot-water vapor, and particulates and free radicals.
- Develop an overall life-threat analysis method that incorporates the effects of heat, toxicity, and smoke obscuration.
- Investigate the factors that influence survivability. Determine physiological and psychological considerations that may determine why some passengers survive. Determine how people are actually affected by the fire environment using data from post-crash survivors as well as fatalities.
- Review methods for assessing irritancy and determine if these methods are meaningful.
- Determine the relationship between physical exertion and adrenaline, alcohol, and other agents on toxic-gas models.
- Examine the relationship between animal models and human responses. To minimize the use of animals, investigate the use of in vitro (or cell culture) methods that can be used instead of whole animals.
- Determine the feasibility of new materials with additives that act as toxicant suppressants.

Special Comments by Marcelo Hirschler

Marcelo Hirschler, a participant in the Toxicity session, submitted the following comments.

The major issue in fire toxicity is that the toxicity of the new materials, when incorporated into the products they will be used in, must not become the limiting factor in the fire hazard associated with the scenario under investigation. The toxic hazard must be assessed as a part of an overall fire hazard assessment.

The major fire scenarios of importance in aircraft are (1) a post-crash pool fire resulting from ignition of aircraft fuel penetrating into the cabin following aircraft skin rupture; (2) a concealed in-flight fire that is not detected for some time; and (3) an open in-flight fire, which is likely to be detected rapidly and will be of little consequence.

In the pool-fire scenario, the incident flux varies about 100-150 kW/m² very close to the rupture point and 10 kW/m² within a relatively short distance from it, which is very different from the approach of a typical flashover fire in ground fires. In aircraft fires, toxicity in a post-flashover scenario is of no consequence, because after flashover aircraft egress is impossible.

Toxicity should be measured by exposing products (and not materials) in a scenario representative of the way in which those products are likely to be exposed within the aircraft.

Any small-scale (or bench-scale) tests to be used must be validated against tests conducted in three other full-scale tests: testing of a complete product in isolation (for example, a chair) or of an entire cabin. These large-scale tests should be the same ones conducted to assess all other fire performance issues.

There should be no prescriptive requirements for toxicity alone, since such requirements may result in eliminating materials that would provide lower fire hazard once the overall fire hazard assessment is conducted.

There is, at present, no fire toxicity requirement by the Federal Aviation Administration, and Mr. Hirschler does not recommend such a requirement. There are requirements set out for some toxic gases, but he does not recommend this method.

None of the existing fire-toxicity test methods are fully acceptable (or capable of achieving consensus). Whatever validated test method is chosen for use must expose products, and determinations should include individual time profiles of individual decomposition products (asphyxiants, irritants, smoke obscuration and temperature). These should then be incorporated (after consideration of the quantity of product present in the fire scenario and the time when the product becomes involved in the fire) in the fire hazard assessment model.

In order to ensure that products with unusual toxicity are not introduced, limited testing of animals (of species for which the toxic effects are known to be relevant to human lethality) should be conducted.

Incapacitation may occur before lethality but is difficult to characterize experimentally. This should be understood and corrections may be needed.

If animal experiments have shown that no unusual toxic effects are present, mass-loss rate may be a first-order approximation to fire toxicity.

Research should include the following:

- investigation of effects on humans, both survivors and fatalities, from actual aircraft fires;
- development of a smoke toxicity test with proven validity for aircraft scenarios;
- potential investigation of effects due to hot-water vapor, particulates, and free radicals;
- potential investigation of in vitro methods for toxicity targets; and
- investigation of potential chronic effects of acute exposures to fire.

Session II:

Fire Performance Parameters

SESSION OBJECTIVES

Determine the fire performance parameters that need to be considered for specifying materials and on what they can be based.

PARTICIPANTS

Chair:	Richard Gann, *National Institute of Standards and Technology*
Committee:	Frederick Dryer, *Princeton University*
	Howard Emmons, *Harvard University*
	Patricia Tatem, *Naval Research Laboratory*
Participants:	Joni Arnold, *Federal Aviation Administration*
	Steven Beare, *DuPont*
	Robert Buch, *Dow Corning*
	Dougal Drysdale, *University of Edinburgh*
	Sally Hasselbrack, *Boeing Commercial Airplane Group*
	Vahid Motevalli, *Worcester Polytechnic Institute*
	Thomas Ohlemiller, *National Institute of Standards and Technology*
	James Quintiere, *University of Maryland*
	Gus Sarkos *Federal Aviation Administration*
	Usman Sorathia, *Naval Surface Warfare Center*

SESSION REPORT

Many of the session participants believed that the measures of fire performance of aircraft interior materials should be consistent with an overall fire hazard analysis.

Fire Performance Parameters

For current aircraft and materials, the Federal Aviation Administration (FAA) Technical Center has demonstrated that the environment within a passenger cabin becomes untenable as the fire changes from localized to full-cabin in extent. Delaying this transition results in longer time for evacuation. Should this determination hold for future aircraft, then the Federal Aviation Administration goal of a 50 percent reduction in fire deaths could be achieved by using materials that further delay or even prevent "flashover."[1] It must also be established that a lethal or incapacitating atmosphere does not exist prior to flashover.

There are conditions that can lead to passengers being unable to evacuate: high temperature, excessive thermal radiation (causing death by burns), and inhalation of toxic gases. The length of exposure to these conditions could be increased by the formation of sufficient amounts of smoke particles and aerosols so that vision is hindered and evacuation is impeded. The potential for the production of corrosive smoke was not addressed. Corrosivity does not affect life safety but may compromise the re-use of the aircraft.

The importance of each threat depends on the time frame for its manifestation relative to the timing of other catastrophic events and the time needed for evacuation. Thus, the type of fire determines which types of materials performance measures are valid. To illustrate this point, the participants considered two classes of fire scenarios (post-crash, fuel fires and in-flight fires) and their variations.

Plane on the ground; external fuel fires; one or more holes in the fuselage; only flame radiation enters. Interior materials are subjected to piloted radiation-induced ignition.[2] Should a seat or interior panel begin burning, then the next important event is the subsequent ignition and burning of adjacent entities. A model of the ignition and fire growth (especially of a seat/assembly) and the transition to more extensive burning of these fire-hardened materials would relate the discrete materials performance measurements to the system behavior. Some of the important properties can be identified from existing knowledge. The model development should be guided by and validated using real-scale tests.

The rate of heat release is the principal driver of fire growth. This can be measured using a device such as the Cone Calorimeter. For low heat release rates, the oxygen depletion may be too small, and an alternative measure based on, for example, CO/CO_2 yield may be necessary. Some participants noted concerns that any bench-scale device may produce artificial phenomena that do not occur at real scale or may miss phenomena that do (e.g., panel buckling and delamination). These concerns will require some testing using larger samples and eventual real-scale testing to resolve. It is important that typical values of the incident radiant flux be obtained from real-scale testing.

According to participants, no current testing device has been shown to give a measure of visual obscuration indicative of the real-scale fire. While the smoke-yield data can be related to visual obscuration via a simple model, it is not yet understood how to use this data in a meaningful way for fire scenarios expected for aircraft.

The radiant smoke toxicity apparatus (ASTM E-1678) measures yields of toxic products that have been related to real-scale fires. In that apparatus, the samples are exposed as in this fire scenario. Other toxic potency methods have not been related to real-scale fires. Analysis of

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[1] A more precise definition of the flashover phenomenon is needed to characterize properly the threat to life safety.

[2] While it is presumed that the aircraft interior materials will be fire-hardened, passengers' clothes and carry-on items will be readily ignited by the high flux.

compartment fires has shown that for combustibles of normal toxicity, heat is the initial threat to life safety. Thus, the premium may well be on determining only if the smoke is of extreme toxic potency.

An additional hazard is that exposure to the fire's hot upper gas layer may cause the ceiling materials to melt, drip, or fall down. This could cause further ignition of interior materials. There is no current measurement method to characterize the physical stability of the installed panels.

Plane on the ground; external fuel fire; one or more holes in the fuselage; flames and smoke enter. In this case, the upper layer of the cabin is quickly vitiated, and thus the decomposition of the exposed panels is different. This could result in a longer flame extension from any burning materials, as well as smoke of higher toxicity, which results from less complete combustion. In the case of vital upper layer, measurements from the above scenario should be supplemented with the yield and flammability limits of the pyrolyzate. There is no procedure for measuring pyrolyzate yield and flammability limits today. The external flames would drive spread on the ceiling, while fire growth over the seats would likely be less important.

Plane on the ground; external fuel fire; no holes in fuselage. The heating of the airplane skin will eventually heat the back side of the interior wall panels, resulting in some degree of aerobic pyrolysis. At the same time, there is a threat that the flames will burnthrough the fuselage, resulting in a fire like the two types described above. Representing the former process will require data on the pyrolysis rates under varying thermal stresses, as well as measurement of the toxicity of the pyrolyzate. Since the fuel fires following a survivable crash have (to date) heated only part of the fuselage, participants thought it likely that evacuating through one or more doors would be practical. Thus, effective hull protection that stays in place could provide ample egress time, and a comparison of the time to appreciable heating and degradation of the wall panels with the time for evacuation is important. Measurement of the insulation system quality is thus an important materials evaluation.

Plane in flight; fire starts within the cabin or lavatory. Participants regarded this as a secondary problem. A small, accessible fire is quickly suppressed with hand-held extinguishers.

Plane in flight; fire starts in an inaccessible area (cargo hold or behind cabin linings). For such a fire, the tenability of the cabin would have to be maintained for up to 3 hours. Should a suppression system not be installed or should it not work, this would require palette containment materials and cabin isolation materials of extraordinary fire resistance. Fortunately, the air leakage into the cargo hold could be made quite small, limiting the burning rate of the combustibles. Research should be conducted to determine whether such materials are possible.

The current test method for the cabin liners is very severe, involving resistance to an intense burner impingement.

Due to increased use and complexity of electronic controls and systems, participants thought that future planes will likely have more electrical cabling running behind the wall panels and under the floors. There is always the potential for ignition in concealed spaces from an electrical fault or an overheated wire. The nearby materials would be exposed to a sustained, but small, hot spot or flame. Participants thought the fire resistance of current materials is probably adequate to survive this threat. Moreover, there has been a lot of work on materials resistance to small ignition sources, so this may not be a research but an implementation issue.

Needed Development in Materials Evaluation and Characterization Methods

The above sections describe the need for characterization of the finished products in order to enable evaluation of their appropriateness for use on board aircraft. A second series of characterizations are those needed for guiding the development of new materials. Participants saw this as especially important in the early stages of exploration where only small (gram) samples of the polymer may exist. Of particular importance is understanding how to promote the formation of char during burning. Some present research includes experiments with the use of techniques such as solid-state NMR for analyzing the partially combusted sample and its char. Participants knew of no existing procedure for screening fire properties through tests on subgram samples. However, research on thermogravimetry and differential scanning calorimetry coupled with mass spectroscopy is investigating the relationship between rate of heat release and ignition behavior. Participants foresaw a critical advance in the characterization of a material's fire contribution when such an appraisal can be based on the molecular chemistry and thermal embodiment of the product. Such relationships, based on fundamental understanding, will enable efficient screening of new materials design.

At present, all materials properties are measured using "new" samples. Aircraft interior products stay in service for years, undergoing wear and tear, frequent cleaning and maintenance, and general aging. It is important that methods be developed for accelerated aging of new materials and structures, so that tests may be conducted to ensure they will retain their desirable fire performance throughout their service life.

As noted above, participants said that several devices are needed to obtain the full complement of data from burning materials for use in a hazard model. It would reduce the burden of testing and increase the reliability of results if a single device were developed to measure parameters such as heat release and smoke obscuration.

Long-Term Research

Participants in the workshop session suggested the following areas for research on fire performance of materials.

- Develop methods for predicting fire performance of materials from chemical structure.
- Develop methods for accelerating materials aging for predicting long-term flammability.
- Develop a verified computer model of ignition of and upward flame spread over low-flammability seats and wall panels.
- Develop accurate bench-scale methods to generate proper materials data.
- Develop new, very small sample guidance methods.
- Develop a validated two-dimensional or three-dimensional model of the evolution of habitability of the cabin environment to identify key materials parameters.
- Develop an understanding of flame spread in a vitiated upper layer and its impact on ignition of fire-hardened seats and wall panels, as well as of clothing and carryon items.

Session III:

Drivers for Materials Development

SESSION OBJECTIVES

Determine the drivers for development and application of advanced fire-resistant materials.

PARTICIPANTS

Chair:	Dennis Nollen, *DuPont*
Committee:	James Peterson, *Boeing Commercial Airplane Group*
	Bruce DeBona, *Allied-Signal*
Participants:	Fred Arnold, *Federal Aviation Administration*
	Donald Cardis, *Schneller, Inc.*
	George Danker, *Akro Fireguard Products*
	Thor Eklund, *Federal Aviation Administration*
	Michael O'Donnell, *Imi-Tech*
	Swen Schaich, *Deutsche Aerospace Airbus*
	Martin Spencer, *Heath Tecna*
	Martel Zeldin, *City University of New York—Staten Island*

SESSION REPORT

Current Fire-Resistant Materials

Just as different materials have varying weight, cost, processability, and availability, they also have varying fire resistance. For example, highly fire-resistant materials include polybenzimidazoles, polyquinoxalines, polyphosphazines, polyimides, phenolics, polyetherketoneketones, polyetheretherketones, ceramics, and metals. Materials that have been modified to meet current regulations include epoxies, polyesters (e.g., Trevira®), and polyurethanes (with carbon).

Aircraft interiors are today made of materials of varying fire resistance, depending on application and materials availability. Typical applications and current materials usage are summarized in the following table. However, many of the available highly fire-resistant materials find limited application in aircraft interiors because of the requirements for aircraft interiors such as weight, cost, manufacturability, and end-use suitability.

Applications	Materials
Floor and floor covering	Glass or carbon/epoxy or phenolic/Nomex® honeycomb floor panels - flexible urethane seat track covers - urethane foam edge band Mylar® film over galley and entry floor panels Wool or nylon carpet - double-backed tapes to attach carpet to floor - Nomex® felt underlay (at customer request) Polyvinylchloride galley mats
Lower sidewall panel	Glass or carbon/phenolic/Nomex® honeycomb plus scuff-resistant surface (wool or Nomex® fabric, or tough plastic)
Upper sidewall panel	Glass or carbon/phenolic/decorative thermoplastic layer plus Tedlar®
Light covers	Polycarbonate
Overhead stowage bins	Glass or carbon/phenolic/Nomex® honeycomb plus edge urethane foam layer plus reinforcement
Gap fillers	Silicone or urethane
Passenger seats	Wool, wool/nylon, or leather upholstery Urethane foam cushions Polybenzimidazole or Nomex®/Kevlar® blocking layer Polyethylene form flotation foam Thermoplastic seat trays
Cabin attendant seats	Wool, wool/nylon, or leather upholstery Urethane foam cushions Polybenzimidazole or Nomex®/Kevlar® blocking layer Polyethylene foam flotation foam
Partitions	Glass or carbon/phenolic/Nomex® honeycomb Decorative thermoplastic laminate or wool/Nomex® textile or leather Polycarbonate transparent wind screen (infrequent)
Stowage bins	Glass or carbon/phenolic/Nomex® honeycomb Decorative thermoplastic laminate Wool textile interior liner (infrequent)
Placards	Polyvinylchloride or urethane
Insulation	Fiberglass batt, phenolic binder, Mylar® cover Polyvinylchloride/nitrile rubber, polyethylene, foams Polyimide foam
Windows	Outer pane stretched acrylic Inner pane cast acrylic Dust cover polycarbonate or acrylic

Applications	Materials
Passenger service units	Molded thermoplastics (Ultem®, Radel®, PEKK) Aluminum Glass or carbon/phenolic
Hoses	Silicone Nylon Urethane
Air ducting	Glass/phenolic, epoxy, or polyester for large ducts Polyisocyanurate foam for large ducts Fire-retarded nylon Glass/silicone Nomex® felt (small quantity) Polyimide foam wrap

For non-aircraft applications, materials are generally used according to the requirements of the application. For many commercial applications, such as buildings, the fire resistance requirements are not very stringent, so the materials used have less fire resistance than those used in aircraft applications. In specialty high-cost and vulnerable items such as manned space vehicles and submarine applications where fire is an extreme hazard, materials that are more fire-resistant are used.

Design and Performance Requirements for Interior Materials

Design and performance requirements were not addressed in this session. The participants felt that the conference papers on this subject by Hanns-Jöerg Betz, Swen Schaich, and Hans-Dieter Berg were complete treatments of these topics.

Goals for Fire Performance of Future Materials

Performance goals for improved materials for future applications were suggested by participants. Commercialization of any new material for aircraft interiors requires, in addition to flammability characteristics, economic viability, consistent manufacturing base, pleasing aesthetics, cleanability, and low-smoke and toxic product emission.

No Flashover. Full-scale tests conducted by the Federal Aviation Administration showed that after flashover, escape from a post-crash fuel-fed fire was no longer possible. Thus a critical step in improving survivability is to preclude flashover.

Uniform Requirements. Standardizing flammability requirements for all interior parts would make materials selection simpler and would reduce the testing and development costs.

However, this would probably limit the availability of materials for the less critical applications, since all materials would have to conform with the most stringent requirements.

Improved Burnthrough Resistance. Glass- and carbon-reinforced sandwich panels already have adequate burnthrough resistance. Other materials could be substituted if their burnthrough resistance was upgraded.

Retention of Mechanical/Physical Properties. Retention of physical and mechanical properties of interior furnishings is important in maintaining the physical integrity of the fuselage, which is crucial for passenger escape.

Totally Nonburnable Materials. If totally nonburnable materials were developed that were also appropriate for aircraft use, fire safety would be upgraded to the highest possible level.

Enclosed Air Circulation Systems. If materials could be adapted to enclose air circulation systems and implemented within acceptable design constraints, fire containment could be improved.

State of the Materials and Fabrication Industries

Although there is still adequate research capability within the materials and fabrication industries, there has been a substantial curtailment of research capability over the past few years with the downsizing of aerospace materials research. This is in part due to a downturn in the defense industry activities and in part due to a downturn in the commercial aviation business. For the materials industry to be able to respond effectively to the challenge of new materials development in a unilateral way, there must be a clear signal that the effort will be supported at government levels on a long-term and sustainable basis. Without this, there is a serious question whether companies would be willing to commit their resources to such research. The fabrication industry in turn will have to wait until materials are available before it can learn how to fabricate parts from such materials.

Drivers and Barriers for the Development of Improved Materials

Session participants identified drivers for, and barriers to, the development and implementation of new materials in commercial aircraft interiors. These are enumerated in the following sections.

Drivers

- The U.S. Congress recognized the need to pursue air travel fire safety by directing the Federal Aviation Administration to establish research and development in this area.
- Materials suppliers and researchers are driven by the potential for a return on investment. If materials with higher fire safety are developed, the developer will expect to obtain return on investment.
- Regulations provide a legal mandate that must be satisfied. If a material being used causes a part to be noncompliant with new rules, changes must be made. Also, the potential of anticipated future regulation would cause material manufacturers to consider working on new materials in anticipation of a potential future profit.
- Differences in regulations among worldwide regulatory agencies tend to drive the implementation of materials and structures that are compliant with the most stringent requirements, since the use of multiple materials for a common application is costly. There has been a substantial effort to develop common regulatory requirements across national boundaries (e.g., Federal Aviation Administration/ JAR, etc.).
- Life-cycle costs have been getting more attention recently. The effort to reduce the cost of ownership for the airlines is a significant factor in the implementation of new technologies. Life-cycle costs can be affected by material costs, fabrication costs, or maintenance requirements.
- Materials with good in-service experience tend to see increased usage. Materials with poor in-service experience or with histories of failures tend to be replaced in subsequent design cycles.
- Aircraft manufacturers have applied new materials unilaterally for many years to provide product improvement or lower costs. Technologies that provide product/process simplification while satisfying other in-use requirements will have priority.
- Weight reduction is a significant driver in aircraft design. Implementation of a material that satisfies other in-use requirements at lower weight is favored.
- Developments that have been funded with government or aircraft industry research money are more likely to be implemented.
- If a manufacturer spends research money to develop a material, there is a strong motivation to receive a return on the investment.
- Both competition and partnerships work to foster further development.

Barriers

Several barriers result from the way that the aircraft manufacturers do business.

- Since cabin designs are upgraded with the introduction of each new aircraft model, there are multiple designs for functionally similar parts with divided manufacturers resisting technologies that were "not invented here."

- Because of the aircraft industry's stringent engineering requirements, certification procedures, expensive quality control, and part configuration control, changes to existing designs are very difficult and costly.
- The cyclic business environment of aircraft manufacturers causes serious problems in materials manufacturers' ability to sustain long-term efforts in materials development.

The nature and size of the market cause problems with the material suppliers.

- Manufacturer's price is high, because niche materials sold at low volume are expensive. It is very difficult to achieve implementation of a new, higher-cost alternative without tangible, quantifiable benefits.
- Without alternative uses for new developments to increase utilization, justifying development of new materials for the limited market will be difficult.
- Aircraft manufacturers are implementing shorter order-to-delivery time, decreasing the time available to implement new materials in a production cycle.
- The high cost of qualification and certification of a new material for aircraft applications makes embarking on a material development and implementation program risky for both the materials supplier and the aircraft manufacturer.
- Downsized industry research organizations will have more difficulty performing the work necessary to develop and commercialize new materials.

Government research programs can present barriers.

- Inadequate cooperation or teaming among government, industry, and academic organizations inhibit the interdisciplinary exchanges required for substantial progress on fire-resistant materials.
- Underfunded government research initiatives inhibit the initiation of long-term research projects.
- Issues concerning intellectual property rights are barriers to joint programs between government, industry, and academia.

It is crucial that there be suitable test procedures and acceptance criteria that have inter-and intralaboratory repeatability and reproducibility. Participants said that the poor reproducibility of current regulatory test procedures have caused, and are still causing, extreme problems.

Long-Term Research

- Make long-term research a priority.
- Establish acceptance criteria.
- Establish goals and requirements.
- Establish repeatable and reproducible test equipment and procedures.

- Establish joint development programs between government, academia, and industry.
- Encourage development through prioritized government grants and contracts to industry and academia.
- Establish a forum for exchange of ideas and results.
- Explore alternative design concepts.
- Explore simplified configuration control possibilities for aircraft manufacturers.
- Explore cooperative ventures between the Federal Aviation Administration and other government agencies.
- To make investment in fire-resistant materials more attractive, expand markets by finding alternative uses for advanced materials, advanced materials concepts, and advanced materials systems.
- Explore promising technologies to improve existing materials, and to develop new materials, modified materials, and hybrid approaches. Suggested activities include new approaches to construction principles, testing, analytical modeling, and processing.

Session IV:

New Materials Technology

SESSION OBJECTIVES

Determine what new or alternative material technologies can lead to materials and assemblies that are significantly more thermally stable (or fire-resistant).

PARTICIPANTS

Chair:	John Rock, *Amoco*
Committee:	Scott Campbell, *McDonnell Douglas*
	Takashi Kashiwagi, *National Institute of Standards and Technology*
	James McGrath, *Virginia Polytechnic Institute*
Participants:	Hans-Dieter Berg, *Deutsche Aerospace Airbus*
	Hanns-Jöerg Betz, *Lufthansa German Airlines*
	Alan Van Buskirk, *General Plastics*
	Kathryn Butler, *National Institute of Standards and Technology*
	Peter Guard, *Boeing Commercial Airplane Group*
	Jeff Gilman, *National Institute of Standards and Technology*
	Theo Klems, *Airbus Industries*
	Menachem Lewin, *Polytechnic University*
	Richard Lyon, *Federal Aviation Administration*
	Dale Onderak, *Schneller, Inc.*
	Edward Weil, *Polytechnic University*
	William Weltner, *M. C. Gillfoam Corporation*

SESSION REPORT

State of the Art of Fire-Resistant Materials

Most materials currently used in new construction in aircraft interiors significantly exceed regulatory requirements. While materials exist that may offer improved fire performance, implementation has been inhibited by unproven economic or technical feasibility.

Current test methods show wide variability and are not predictive of large-scale performance. The results from these tests provide little guidance in the development of new materials or the improvement of existing materials.

Materials Fire Performance Goals for Long-Term Research

Participants agreed that the current goal for long-term research should be to improve the fire performance of materials by an order of magnitude. Specific goals include:

- increasing fire resistance (e.g., reduce heat release to zero for 5-10 minutes at 35 kW/m², external flux);
- delaying or preventing ignition; and
- minimizing toxic products (both in processing/fabrication and burning).

Other specific goals suggested by participants are to develop small-scale tests that better correlate to large-scale tests and to actual fire scenarios and to assess the benefit of improvements in fire performance of materials (i.e., perform cost-benefit analysis on potential improvements).

Promising Materials Technologies or Approaches

In general, two approaches to more fire-resistant polymeric materials development are possible: polymers with additives that make them fire-resistant and fire-resistant polymers that do not require additives.

Approaches that show particular promise include:

- thin, laminated or co-extruded films and blends,
- coatings and additives (especially intumescents),
- phase-change or temperature-sensitive ("intelligent") materials,
- organic-inorganic polymer blends, and
- polymer modifications.

Needed Development in Materials Science and Characterization Methods

In order to facilitate the development and commercialization of improved fire-resistant materials and structures, many of the group agreed to the following suggestions.

- Develop lower-cost processing and scale-up methods for existing specialty materials.
- Develop processes and methods to incorporate reflective layers or coatings into structures.
- Advance the understanding and science base in the areas of ignition and char formation.
- Develop computational tools and models as guidelines for basic polymer science.

Long-Term Research

Session participants suggested the following areas for long-term research.

- Develop a basic scientific understanding of char and intumescence. Include research in char formation, with investigations into the effects of atmosphere, heating rate, chemical derivitization, additives, and coatings, as well as in char characteristics such as mechanical behavior (durability) and solid-state structure.
- Develop a basic scientific understanding of ignition behavior.
- Investigate development of improved materials for next-generation aircraft interiors. There are three directions for materials development:

    1. Modification of engineering polymers such as polycarbonate, nylon, polyethyleneterephthalate, phenolic, and wool to improve fire resistance; these may represent the lowest-cost alternative.
    2. Development of a greater understanding of thermal degradation mechanisms of specialty polymers (with or without additives) such as polyetheretherketone, polyetherimide, polyphenylenesulfide, and polysulfone; these should represent the best performance in the near term (≤10 years).
    3. Development of high-performance, thermally stable materials including organic-inorganic systems, copolymers, polymer blends and alloys, and glasses and ceramics; these represent the best performance in the long-term (≥ 10 years).

- Research low-cost manufacturing technology for the "most-promising" materials.
- Give primary priority to composite fibers and thermoplastic and thermoset matrices; materials and processes from thermoplastic molding and thermoforming; decorative layers including varnishes, foils, and thermoplastics; foam-core materials and nonmetallic and aluminum honeycomb materials, textiles; and adhesives.
- Give secondary priority to transparencies; glass fiber, carbon fiber, and foam insulations; electronics; wire and cable; and elastomers.

Appendix A

Conference Program on Fire and Smoke Resistant Materials

National Academy of Sciences
2101 Constitution Avenue, NW
Washington, D.C.

November 8-10, 1994
Tuesday, November 8

8:30	Conference Introduction Eli M. Pearce, *Polytechnic University*
9:00	Federal Aviation Administration Fire Safety Mission Thomas E. McSweeny, *Federal Aviation Administration (FAA)*
9:30	Airplane Accidents and Fires Thomas M. Murray, *Boeing Commercial Airplane Group*
10:00	Heat Exposure and Burning Behavior of Cabin Materials During an Aircraft Post-Crash Fuel Fire Constantine P. Sarkos, *Federal Aviation Administration, Technical Center*
11:00	Fundamental Fire Properties of Combustible Materials Dougal D. Drysdale, *University of Edinburgh*
11:30	Fire Tests and Hazard Evaluation James G. Quintiere, *University of Maryland*
12:00	Fire Properties of Materials Archie Tewarson, *Factory Mutual* (presented by Ronald Alpert, *Factory Mutual)*
1:30	Fire-Screening Results of Polymers and Composites Usman Sorathia, *Naval Surface Warfare Center, Carderock Division*
2:00	Fire Properties of Future Material Candidates Charles A. Wilkie, *Marquette University*

2:30	Meeting FR Goals Using Polymer Additive Systems Edward D. Weil, *Polytechnic University*
3:30	Developments in Thermally Stable Polymers Paul Hergenrother, *National Aeronautics and Space Administration, Langley Research Center*
4:00	An Overview of Inorganic and Organometallic Polymers Martel Zeldin, *City University of New York-Staten Island*
4:30	Flame-Retarding Wool Textile Materials and the Evaluation of Thermally Stable Polymers for Commercial Airplanes Sally A. Hasselbrack, *Boeing Commercial Airplane Group*
5:00	ADJOURN
Wednesday, November 9	
8:30	Smoke Toxicity David Purser, *Fire Research Station, United Kingdom*
9:00	In-Service Performance Criteria for Aircraft Hanns-Jöerg Betz, *Lufthansa German Airlines*
9:30	Design of Aircraft Interiors Swen J. Schaich, *Deutsche Aerospace Airbus*
10:00	Processing and Manufacturing of Interior Components Hans-Dieter Berg, *Deutsche Aerospace Airbus*
10:30	Charge to Workshop and Logistics Eli M. Pearce, *Polytechnic University*
11:00	Breakout Sessions **Session I - Toxicity Issues** Session Chair: Stephanie Skaggs, *New Mexico Engineering Research Institute* **Session II - Fire Performance Parameters** Session Chair: Richard Gann, *National Institute of Standards and Technology* **Session III - Drivers for Materials Development** Session Chair: Dennis Nollen, *DuPont*

	Session IV - New Materials Technology Session Chair: John Rock, *Amoco*	
5:00		ADJOURN
Thursday, November 10		
8:30	Prepare Workshop Reports	Breakout Groups
10:00	Present Findings of Breakout Groups	Session Chairs
12:00	Discussion of Conclusions	All
1:00	ADJOURN	

Appendix B

Conference Participants and Speakers

Participants

Fred Arnold, Federal Aviation Administration, Atlantic City, New Jersey

Joni Arnold, Federal Aviation Administration, Atlantic City, New Jersey

Steven Beare, Senior Research Associate, DuPont Advanced Fibers System, Wilmington, Delaware

Robert Buch, Senior Research Specialist, Dow Corning Corporation, Auburn, Michigan

Gary T. Burns, Associate Research Specialist, Dow Corning Corporation, Midland, Michigan

Kathyrn M. Butler, Physicist, National Institute of Standards and Technology, Gaithersburg, Maryland

Daniel Caldwell, U.S. Army Medical Research and Development Command, Tri-Service Toxicology, Wright-Patterson Air Force Base, Ohio

Donald R. Cardis, President and CEO, Schneller, Inc., Kent, Ohio

George J. Danker, Vice President - Chief Technical Officer, Akro Fireguard Products, Lenexa, Kansas

Richard G. Gann, Chief, Fire Science Division, National Institute of Standards and Technology, Gaithersburg, Maryland

Jeffrey W. Gilman, Research Chemist, National Institute of Standards and Technology, Gaithersburg, Maryland

Peter S. Guard, Manager, BCAG Color and Material, Boeing Commercial Airplane Group, Issaquah, Washington

Marcelo Hirschler, Safety Engineering Laboratories, Rocky River, Ohio

Theo Klems, Senior Engineer, Airbus Industries, Blagnac Cedex, France

Sheldon Lapan, Research Epidemiologist, Maryland Center for the Study of the Health Effects of Fire, Baltimore, Maryland

Menachem Lewin, Professor, Polymer Research Institute, Polytechnic University, Brooklyn, New York

Nelson Miller, Director, Aircraft Safety, Federal Aviation Administration, Atlantic City, New Jersey

Vahid Motevalli, Visiting Professor, George Washington University, Washington, D.C.

Dennis Nollen, DuPont Advanced Materials Systems, Newark, Delaware

Michael O'Donnell, Tech Sls. Manager, Imi-Tech Corporation, Mt. Vernon, Washington

Thomas J. Ohlemiller, Chemical Engineer, National Institute of Standards and Technology, Gaithersburg, Maryland

Dale G. Onderak, Vice President, Research and Development Tech Service, Schneller, Inc., Kent, Ohio

Milo Raub, Manager, Systems and Interiors Engineering, Trans World Airways, Kansas City, Missouri

John A. Rock, Staff Scientist, Amoco Polymers, Alpharetta, Georgia

Henry J. Roux, President, Roux International, Inc., Lancaster, Pennsylvania

Kelley Scott, Analyst, U.S. Congress, Office of Technology Assessment, Washington, D.C.

Stephanie Skaggs, Deputy Director, Center for Global Environmental Technologies, New Mexico Engineering Research Institute, Albuquerque, New Mexico

Joseph R. Soderquist, Chief Scientific/Tech Advisor, Federal Aviation Administration, Washington, D.C.

Martin Spencer, Heath Tecna Aerospace Company, Bellingham, Washington

Guiliana Tesoro, Research Professor, Polytechnic University, Brooklyn, New York

Allan Van Buskirk, Research Chemist, General Plastics Manufacturing Company, Tacoma, Washington

William F. Weltner, Development Manager, M.C. Gill Corporation, El Monte, California

Bob Williams, Interior Systems Engineer, Delta Air Lines, Atlanta, Georgia
Mike Williams, Group Leader Manager, Interior Design for McDonnell Douglas, Long Beach, California
Chuck Williamson, QA Manager, General Plastics Manufacturing Company, Tacoma, Washington

Speakers

Hans-Dieter Berg, Deutche Aerospace Airbus, Bremen, Germany
Hanns-Jöerg Betz, Lufthansa German Airlines, Frankfurt, Germany
Dougal D. Drysdale, University of Edinburgh, Edinburgh, Scotland
Sally A. Hasselbrack, Boeing Commercial Airplane Group, Seattle, Washington
Paul Hergenrother, National Aeronautics and Space Administration, Langley Research Center, Hampton, Virginia
Thomas E. McSweeny, Aircraft Certification Service, Federal Aviation Administration, Washington, D.C.
Thomas M. Murray, Boeing Commercial Airplane Group, Seattle, Washington
David Purser, Fire Research Station, Watford, United Kingdom
James G. Quintiere, University of Maryland, College Park, Maryland
Constantine P. Sarkos, Fire Safety Branch, Federal Aviation Administration, Atlantic City, New Jersey
Swen J. Schaich, Deutche Aerospace Airbus, Hamburg, Germany
Usman Sorathia, Naval Surface Warfare Center, Annapolis, Maryland
Archie Tewarson, Factory Mutual Research Corporation, Norwood, Massachusetts
Edward D. Weil, Polytechnic University of New York, Polymer Research Institute, Brooklyn

Charles A. Wilkie, Marquette University, Milwaukee, Wisconsin
Martel Zeldin, City University of New York, Staten Island, New York